Colour and Chemical Oxygen Demand Removals in Oxidation of Reactive Blue 19 Using Wet Air Oxidation Catalyzed by Natural Ores

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Four natural ores of iron and manganese (Mn-CB, Mn-HG, Mn-TG, Fe-TC) selected in Vietnam were used as catalysts for oxidation of Reactive blue 19 in catalytic wet air oxidation process (CWAO). The manganese containing ores were found to be very effective for colour treatment (up to 94 %) at 150 °C and 13 bar of oxygen. However they show much lower efficiency in chemical oxygen demand removal with a maximum value of 33 %. That reveals manganese ores only boost partial oxidation of the dye molecule. The iron ore, in another hand, exhibits both low colour and chemical oxygen demand removals but complete destruction of the dye molecule can be achieved. Kinetics of the colour destruction was investigated using Mn-CB ore. The rate of the process can be described by the expression $w = k \cdot [RB19]^a \cdot P_{O_2}^b \cdot [cat.]^c$ with a = 0.55, b = 0.40, c = 1.2 and $k = 2.6 \times 10^{-2}$ ($L^{0.75}$ $mg^{0.45}$ $g^{-1.2}$ $bar^{-0.41}$ min^{-1}).

Keywords: Wet air oxidation, Reactive blue 19, Natural ore, Catalyst, Colour removal.

INTRODUCTION

Pollution by wastewaters from textile industry is a problematic issue in Vietnam. It has been estimated that hundreds of millions m^3 of untreated dye effluents from about 2000 textile mills are discharged into the environment annually. This huge amount of wastewater with strong colour and high chemical oxygen demand values are causing serious effects on aquatic ecological system. Therefore treatment of dye wastewater is urgent demand for improving quality of water body.

Several techniques have been proposed to remove dye stuffs, including physical, chemical, biological processes, membrane filtration and advanced oxidation processes (AOPs)[1-8]. Among these methods, wet air oxidation (WAO) proposed and developed by Zimmerman appears as one of the most effective techniques for removing persistent organic compounds[9,10]. Wet air oxidation is a liquid-phase oxidation process working at elevated temperatures (150-300 °C) and high pressures (up to 200 bar) with the use of oxygen as an oxidant[9,10]. It has been reported to transform organic matters to CO_2 and other end-products[11,12]. Therefore wet air oxidation is more eco-friendly and economical than advanced oxidation processes that require expensive oxidizing agents such as O_3

and H_2O_2. In last two decades, the application of catalysts for wet air oxidation has been received much interest owing to milder conditions and shorter residence time. Up to date, most of catalysts are mixtures of synthesized transition/precious metal oxides[13-19]. But high cost of catalyst production limits the application of catalytic wet air oxidation process in practice. A possible solution for the limitation of high catalyst cost is using natural ores (or modified natural ores). However, up to date, there is no literature available on studying this subject. In order to evaluate catalytic potential of this kind of materials for wet air oxidation, this work using four different natural ores as catalysts for dye treatment in catalytic wet air oxidation process.

EXPERIMENTAL

Four different natural ores containing iron and manganese collected from North of Vietnam were used as catalysts in this study. Before experiments, the ores were grounded and sieved for a fraction of particles less than 45 μm in diameter. X-ray diffraction technique (D8 Advanced Brucker) was used to determine the structures of these materials. Specific areas of the ore samples were measured by BET method (Micromeritics TriStar 3000 V6.07A). For composition characterization, the

ores were digested with a mixture of HNO₃ and H₂SO₄ and then analyzed by atomic absorption spectroscopy technique.

In this work an active dye named Reactive blue 19 (RB19) (Fig. 1) was used as a target compound.
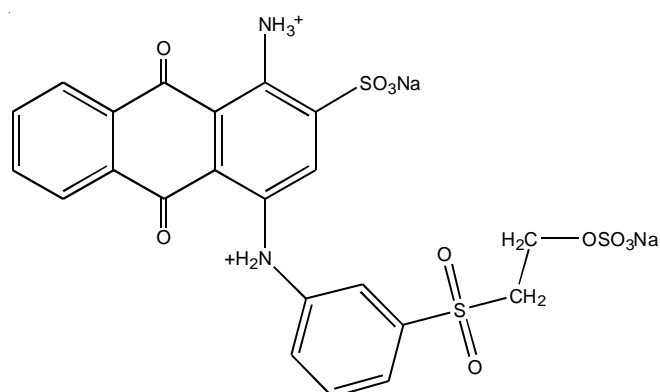

Fig. 1. Chemical structure of Reactive blue 19

Experimental procedure: The oxidation was carried out in 1 L autoclave equipped with a cooling coil and a mechanic stirring system (Parr Instrument). A schematic diagram of the catalytic wet air oxidation system is showed in Fig. 2.
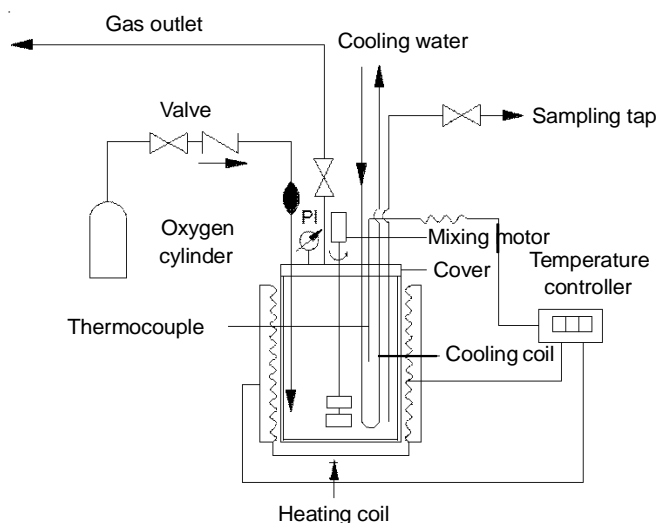

Fig. 2. A schematic diagram of the catalytic wet air oxidation system

Before oxidation, 500 mL of reacting solution containing a given dye content and pre-determined mass of a catalyst was purged with a pure N₂ flow of 1.4 L/min at a total pressure of one bar for 15 min. The solution was constantly stirred at 800 rpm which was chosen to eliminate diffusion kinetics. After purging the temperature of the reactor was raised to 150 °C, pure oxygen was introduced into the system to start the oxidation. During experiment, pressure of oxygen was kept constant at 13 bar. Other conditions of the experiment are given in Table-1. A control experiment was also conducted without the presence of the catalyst under nitrogen atmosphere to confirm no thermal decomposition of the dye.

Liquid 10 mL samples taken at different reaction times were allowed to cool down to room temperature and then were filled through a standard 0.4 μm membrane filter. The filtrates were subjected to determination of dye concentrations and chemical oxygen demand values. Reactive blue 19 displays a maximum absorption at 590 nm. Therefore its concentrations in the samples were determined based on measuring light absorption of the samples and a standard calibration line at this wavelength. The chemical oxygen demand analysis was carried out according to standard APHA method 5220D[20].

Efficiency of the oxidation process at time (t) was expressed as the ratio of removed concentration to the initial concentration of the dye/chemical oxygen demand as following:

$$\eta_t, \% = [(C_o - C_t)/C_o] \times 100$$

where C_o, C_t are values of colour/chemical oxygen demand content at initial stage and after time (t), respectively.

RESULTS AND DISCUSSION

Characterization of catalyst: Characteristics of four selected natural ores are determined and presented in Table-2. The composition results show that the main metal of three ores (Mn-CB, Mn-HG, Mn-TG) is manganese in the phase of α-MnO₂. However, the contents of manganese are quite different, to be 41, 31 and 19 %, respectively. Silicon dioxide, which is known to be inert in catalyst, is present in a large portion, up to 44 %, in these ores. Iron is also found with small contents of less than 8 %. The last ore (Fe-TC) contains largely of iron in the form of α-Fe₂O₃. Specific areas of all ores are determined to be in the range of 23-44 m²/g.

Catalytic activity screening: Before oxidation experiment, adsorption of Reactive blue 19 on four selected natural ores was evaluated in the same conditions of concentrations and temperature as given in Table-1, but in the absence of oxygen to eliminate any catalytic degradation of the dye. The amount

TABLE-1
EXPERIMENTAL CONDITIONS FOR CATALYTIC WET AIR OXIDATION

Parameter	Reaction volume (mL)	Dye concentration (mg/L)	Catalyst concentration (g/L)	Temperature (°C)	Oxygen pressure (bar)
Value	500	760	10	150	13

TABLE-2
CHARACTERISTICS OF FOUR SELECTED ORES FOR CATALYTIC WET AIR OXIDATION

Ore	Compositions (%)				Main phase	S_{BET} (m²/g)
	Fe	Mn	SiO₂	Others		
Mn-CB	6	41	20	33	α-MnO₂	43.5
Mn-HG	3	31	30	36	α-MnO₂	23.1
Mn-TG	7	19	44	31	α-MnO₂	28.4
Fe-TC	49	3	16	32	α-Fe₂O₃	32.3

of the dye adsorbed was found to be less than 10 % of initial concentrations after 3 h. Therefore, depletion of the dye in the catalytic wet air oxidation process process is assumed to be due to catalytic oxidation. The efficiency of dye degradation in this catalytic wet air oxidation process was determined by analyzing dye concentration and chemical oxygen demand value of the reacting solutions at different reaction times. The obtained profiles of dye concentrations and chemical oxygen demand are displayed in Figs. 3 and 4, respectively. In aspect of colour removal, Mn-CB ore shows the highest activity with 94 % of initial dye content removed in 1 h. Both Mn-HG and Mn-TG ores reveal less activity (slower depletion of the dye). However these two ores can attain 90 % of removal after 3 h. Comparing with the compositions of the ores, it can be seen that catalytic activity is proportional to the manganese content. The ore of iron (Fe-TC) was shown to be ineffective. It only removes 30 % of the colour after 3 h.
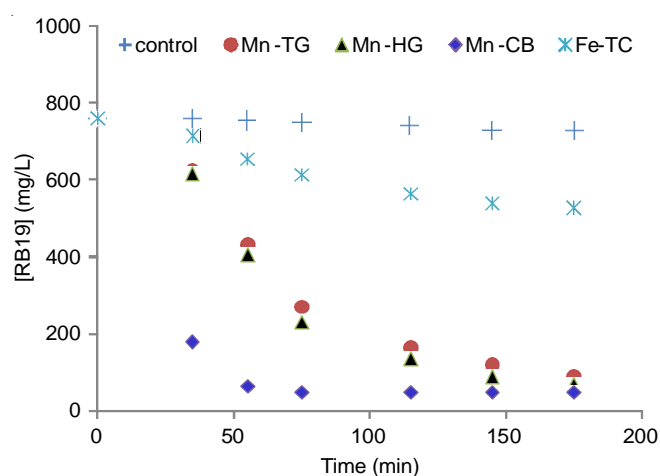

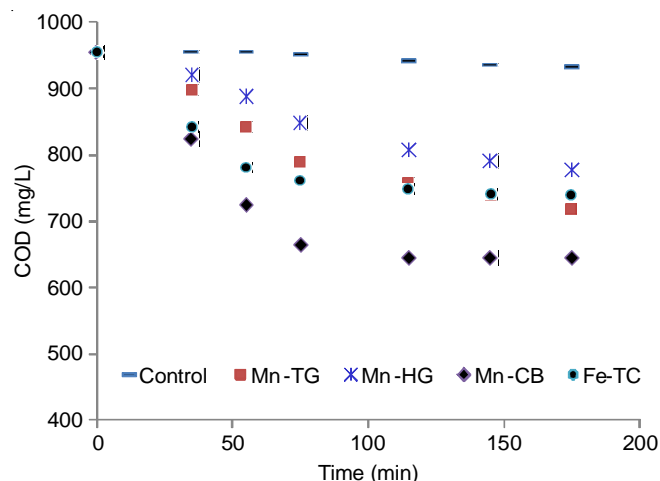Fig. 3. Colour removal in catalytic wet air oxidation

Fig. 4. COD removal in catalytic wet air oxidation

The variations of chemical oxygen demand values with time in Fig. 4 show lower removal efficiencies compared to colour treatment. The order of catalytic activity of the three manganese containing catalysts for chemical oxygen demand treatment is the same as for the colour in the sequence Mn-CB > Mn-TG > Mn-HG. The maximum removal of chemical oxygen demand of only 33 % was obtained using Mn-CB after 3 h. Table-3 presents percentage of initial chemical oxygen

demand removed by other ores. Compared with high colour removal, it can concludes that the manganese containing ores just catalyst for partial oxidation of the dye, in particular to chromophore groups. In case of the iron ore (Fe-TC), efficiency of chemical oxygen demand treatment is close to that of colour removal as can be seen in Table-3. It means that iron oxide can give complete oxidation.

TABLE-3
EFFICIENCIES OF DYE AND CHEMICAL OXYGEN
DEMAND (COD) REMOVAL AFTER 3 h OXIDATION

Ore	Mn-CB	Mn-HG	Mn-TG	Fe-TC
Dye removal (%)	94	91	88	30
COD removal (%)	33	19	26	23

Kinetics of colour removal using Mn-CB ore: In this experiment, Mn-CB ore was chosen for determining kinetics of the catalytic process. The rate of colour disappearance can be described by expression:

$$w = k \cdot [RB19]^a \cdot P_{O_2}^b \cdot [cat.]^c \qquad (1)$$

where [RB19], [cat.], P_{O_2} are concentrations of Reactive blue 19, catalyst and pressure of oxygen, respectively. a, b, c: are the orders of the reaction with respect to Reactive blue 19, O_2 and catalyst. k: rate constant of the oxidation.

TABLE-4
CONDITIONS FOR KINETIC EXPERIMENTS

Order	[RB19] (mg/L)	[Mn-CB] (g/L)	Temp. (°C)	P_{O_2} (Bar)
a	185, 271, 422, 569, 710, 867	3	150	13
b	423	3	150	2, 5, 9, 13
c	423	2, 4, 6, 8	150	13

The rate constant and the orders (a, b, c) were determined using the initial rate method in which initial rate (w_0, mg/(L min)) was derived from variation of dye concentration (ΔC) in a short time (Δt) at the beginning of the reaction $w_0 = \Delta C / \Delta t$. In order to get the value of a, the oxidation was carried out with different initial Reactive blue 19 concentrations in the presence of the same amounts of catalyst and oxygen. In this conditions, a is determined from slope of the plot ln (w_0) *versus* ln ([RB19]). b and c are also determined by the same manner with the changing in oxygen pressure or concentration of catalyst. Obtained natural-log plots for determination of a, b, c are displayed in Fig. 5. From these plots, the orders of the reaction with respect to Reactive blue 19, oxygen and catalyst are given to be a = 0.55, b = 0.40 and c = 1.2.

The rate constant was calculated by the expression:

$$k = \frac{w_0}{[RB19]_0^a \cdot P_{O_2,0}^b \cdot [cat.]_0^c} \qquad (2)$$

An average value of k at 150 °C was calculated to be 2.6 × 10^{-2} ($L^{0.75}$ $mg^{0.45}$ $g^{-1.2}$ $bar^{-0.41}$ min^{-1}).

Conclusion

Catalyst activity of natural ores containing manganese and iron for Reactive blue 19 treatment in catalytic wet air oxidation was investigated in this work. The resulting data show that
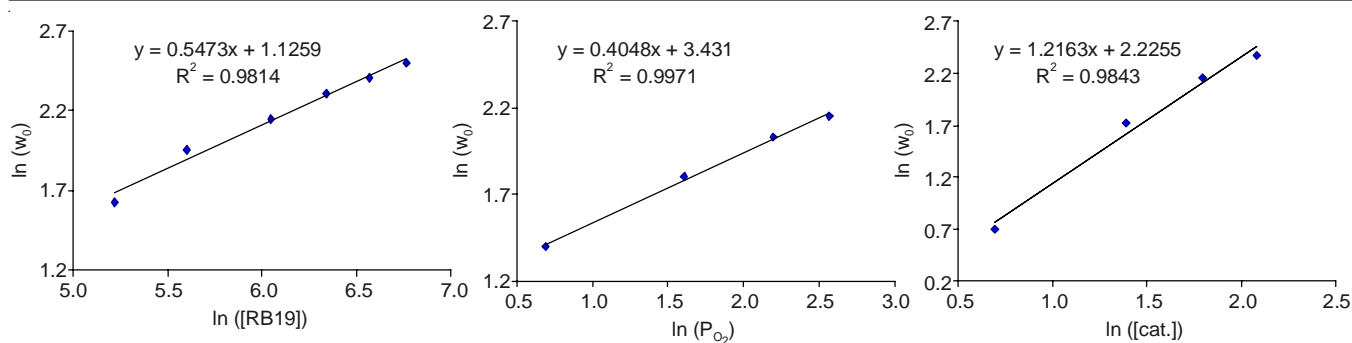
Fig. 5. Natural-log plots for determination of the reaction orders

manganese ores possess high activity for colour degradation but low chemical oxygen demand removal efficiency. The iron ore exhibits low activity for both colour and chemical oxygen demand removal. However, this material can give complete oxidation of the dye molecule. These results demonstrate a potential of using natural ores for catalyst in wastewater treatment. From this observation, we propose a combination of natural-ores-catalyzed wet air oxidation with post biological method for effective treatment of dye containing wastewaters.

ACKNOWLEDGEMENTS

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