



Wet air oxidation of pretreatment of pharmaceutical wastewater by Cu^{2+} and $[\text{P}_x\text{W}_m\text{O}_y]^{q-}$ co-catalyst system

Guowen Wang, Dong Wang, Xiaochen Xu, Lifen Liu, Fenglin Yang*

Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education, China), School of Environmental Science and Technology, Dalian University of Technology, Linggong Road 2, Dalian 116024, China

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ABSTRACT

This study concentrates on the pretreatment of real wastewater using catalytic wet air oxidation (CWAO). WO_3 and PO_4^{3-} contained in fosfomycin pharmaceutical wastewater (FPW) and Cu^{2+} contained in berberine pharmaceutical wastewater (BPW) were studied as CWAO influent. Mixture of these two streams were reused to form Cu^{2+} and $[\text{P}_x\text{W}_m\text{O}_y]^{q-}$, namely polyoxometalates (POMs) as co-catalyst system to treat themselves. Experiments were conducted to investigate the effects of the initial oxygen pressure and temperature on the COD (chemical oxygen demand), TOC (total organic carbon) removal and biodegradable enhancement, it was discovered that over 40% of COD and TOC removal can be easily realized in an hour of WAO oxidation at 523 K, 1.4 MPa. The BOD_5/COD (BOD_5 , biochemical oxygen demand in 5 days) of this two pharmaceutical mixture ascended from nonexistent to maximum 0.41 depends on the optimal FPW:BPW volume ratio 4:1, to compose POM co-catalyst system. Organic pollutants were incompletely oxidized to propionic acid and other intermediates. Some properties (e.g., TGA, IR, XRF) of POM catalyst separated from effluent, were obtained to provide additional information.

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1. Introduction

Tightening environmental legislation is leading the chemical and especially pharmaceutical industries to consider wastewater discharge that needs source separation or overall technology for biological toxics (e.g., antibiotics, interferon) into environmental water [1,2]. CWAO is one of the most attractive technologies for pretreatment in the context of integrated special wastewater or sludge treatment [3], however, the presence of corrosive chemical compounds in the wastewaters along with high temperatures and pressures renders the reaction environment in a CWAO reactor highly corrosive [4]. Fortunately, recent developments in heteropolyacid (HPA) chemistry has led to the polyoxometalates' family application, which is being used in liquidus oxidation, and is important to what is known as clean technologies, hence many of the catalytic activity and corrosion problems of the traditional CWAO are avoided. Within the scope of the literature review, Sonnen et al. [5] studied degradation of pulp-mill effluent by CWAO and $\text{Na}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$ as catalyst, and the result showed that POM can be used under mild conditions (423 K, 0.7 MPa of O_2) to catalyze the wet air oxidation of the dissolved organics. Ishii et al.

[6] demonstrated that oxidations of a wide variety of organic substrates with commercially available 35% H_2O_2 can be effectively performed in homogeneous phase or more often in a biphasic system with the use of a catalyst comprising heteropoly acids PW or PMo and cetylpyridinium chloride. Lately, Zhao et al. [7] have prepared micellar $(\text{C}_{16}\text{TA})_6[\text{PV}_3\text{MoO}_{40}]$ to catalyze phenol in wet oxidation, which showed 95.3% degradation efficiency, 98.5% COD removal and 93.0% TOC reduction with air under room condition in 90 min. Zhang et al. [8] reported the excellent catalytic activity of $\text{Zn}_{1.5}[\text{PMo}_{12}\text{O}_{40}]$ with nanotube structure for the CWAO of Safranin-T, in which a 98% of color and a 95% of COD were removed within 40 min. On the whole, several new-types of homogeneous catalysts of CWAO were in rapid development over recent years [9,10]. Specially, Cu salts were mostly studied due to their high activity and acceptable operating cost compared with precious metals [11–13].

Fosfomycin and berberine pharmaceutical wastewater have the characteristics of high concentration refractory COD, low biodegradability and high ecotoxicity, and their presence in wastewater even in very low concentration is harmful to aquatic life [14], so they were urgent need of addressing pollution. As we wished, these two streams were chosen as target CWAO influent in this study, containing PO_4^{3-} , WO_3 (in FPW) and Cu^{2+} (in BPW) respectively, so that, FPW combined with BPW (mixture with suitable volume ratio) to form a co-catalyst system is challenging. Noteworthy, reusing these active ions to degrade and either

* Corresponding author. Tel.: +86 411 84706172; fax: +86 411 84706238.
E-mail addresses: guowenwang@yahoo.com (G. Wang), yangfl@dut.edu.cn (F. Yang).

Table 1
Main characteristics of fosfomycin pharmaceutical wastewater (FPW).

Parameter	Value
COD (mg/L)	188,108
TOC (mg/L)	46,000
BOD ₅ /COD	Nonexistent
Total phosphorus (mg/L)	30,000
PO ₄ ³⁻ (mg/L)	3000
pH	11

detoxicate organics in wastewater simultaneously, satisfies with demand of treating wastes with wastes.

As demonstrated by Kozhevnikov [15], the nature of counter-cation in polyoxometalates is critical with respect to their acidity, solubility, porosity, and thermal stability. Salts with rather small cations (e.g., Cu, transition metal) resemble the parent heteropolyacids; they are readily soluble in water. However, research in the area of cupric substituted heteropolymolybdates was not taken seriously. Keggin-type vanadium substituted heteropolymolybdates as catalysts for wet oxidation was discovered by Kozhevnikov and Matveev [16,17], in the 1970s, which was the most efficient and versatile catalyst in the polyoxometalate series for oxidation by O₂. In fact, POM were not only economically and environmentally attractive, but also exhibiting fast reversible multi electron redox transformations under rather mild conditions. Their acid base and redox properties can be varied over a wide range by changing POM's chemical composition [18]. For this reason, a series of experiment should be performed to identify suitable catalysts to increase the reaction rate of refractory wastewater at relatively mild temperatures and pressures. Catalysis by polyoxometalates compounds is a field of increasing importance. Even though the previous results have made POM notable in the area of organics oxidation, to the best of our knowledge, the information of cupric salts assembling in [P_xW_mO_y]^{q-} as catalyst in CWAO for waste treatment is still scarce.

The aim of this work was to investigate the synergetic catalytic effect of species in fosfomycin and berberine wastewater, base on the consideration of this, we evaluated the effect of several operating parameters such as reaction temperature, oxygen partial pressure, POM co-catalyst on enhancing the selectivity of the reaction toward more biodegradable by-products. In addition, we seriously discussed reusing of waste for simultaneously treating fosfomycin and berberine pharmaceutical wastewater.

2. Experimental details

2.1. Characteristics of the wastewater

The real wastewater was collected directly from the packet filter and washing process of Northeast General Pharmaceutical Factory (NEGPF) in China, with toxic intermediate product now requiring disposal, has feature as Tables 1 and 2 described. Given the COD and BOD₅ values as well as the pH value, these two streams were untreatable by utilizing biodegradation techniques., that is, it can be defined as a refractory and high concentration pharmaceutical wastewater. Incidentally, the high content of heavy metal (Cu) and

Table 2
Main characteristics of berberine chloride pharmaceutical wastewater (BPW).

Parameter	Value
COD (mg/L)	3201
TOC (mg/L)	1470
BOD ₅ /COD	Nonexistent
Cu ²⁺ (mg/L)	12,790
pH	1

antibiotic species (fosfomycin and berberine) may also contribute to the toxic nature.

2.2. Operation of CWAO reaction

The CWAO experiments were carried out in a 0.5 L autoclave (Model CJF-0.5-1Cr18Ni9Ti, Dalian, China) equipped with stainless steel Swagelok tubes and valves, which allowed the addition of oxygen and the withdrawal of samples during a run, magnetic stirring system ensured good amount of mass transfer among reaction systems. Thermocouple pyrometer has been used to control temperature exactly, and heating was provided by an external heating casing.

Before the start of experiment, FPW:BPW volume ratio set at 225 mL:25 mL, mixture pH 6.2–7.4 and 200 mL:50 mL, mixture pH 3.7–4.3 respectively. The autoclave was then run at (150, 200, 250) ±5 °C respectively. Pure oxygen (1.4 MPa, 0.7 MPa, and 0 MPa) was added initially to meet 15%, 7.5%, and 0% of the theoretical oxygen demand according to the COD value of CWAO influent samples. When operating temperature was attained after 80 min heating, defining the starting time as 0 min, then the influent was stirred for 60 min reaction time, 40 min for cooling time. During the reaction, samples were withdrawn periodically. CWAO experiments were conducted to ascertain the efficacy on COD, TOC removal, and BOD₅/COD enhancement. Therefore, a series of experiments were carried out at different temperatures or initial oxygen pressures. While investigating the temperature and FPW:BPW volume ratio effected on effluent parameters, the initial oxygen pressure was kept at a constant 1.4 MPa for security reasons.

2.3. Analytical methods

The pH, COD, BOD₅, TOC of samples has been taken from the reactor, which was monitored during the course of experiment. COD and BOD₅ were measured with the previous standard methods for wastewater examination to evaluate biodegradability of the wastewater [19,20]. TOC was measured with a Shimadzu 5050 TOC analyzer. An effluent samples were analyzed with Shimadzu GC2010, the details of operation condition temperature for splitless injector and FID detector temperature was 200 °C and 220 °C respectively with splitless ratio 10, inlet pressure 15 kPa, nitrogen carrier gas 0.7 MPa, column temperature 150 °C, FFAP capillary column, 30 m × 0.53 mm, 1.0 μm film thickness. Shimadzu UV-1700 was used to determine short chain volatile organics and UV absorption spectra. Thermal analysis was performed on a Seiko EXSTAR TG/DTA 6300 thermal analyzer using a heating rate of 10 °C/min in an air stream for thermogravimetry. FT-IR spectra were recorded on a Shimadzu spectrometer in KBr pellets over the range of 400–2000 cm⁻¹ under atmospheric conditions without special precautions. Elemental composition of precipitate from effluent sample was determined with Bruker SRS-3400 sequential X-ray fluorescence (XRF) spectrometer. XRD measurements were carried out on a Rigaku D/max-2400 diffractometer operating at a tube voltage of 12 kV. Patterns were recorded over the range from 5° to 70° (2θ) in steps of 0.01° with a count time of 1 s at each point. DO (dissolved oxygen) was measured with YSI 550A DO analyzer.

3. Results and discussion

3.1. The effects of temperature and pressure on COD and TOC removals

The COD and TOC values for CWAO influent (supernatant of FPW and BPW filtered away precipitate) were ca. 121,081 and 58,230 mg/L at the volume ratio of FPW:BPW = 200 mL:50 mL. The concentration of mixture influent COD was partially eliminated by

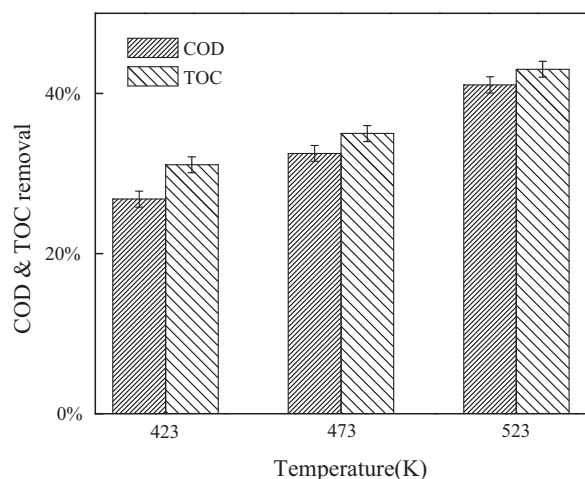


Fig. 1. Effect of temperature on COD and TOC removals (initial O₂ pressure: 1.4 MPa; reaction time: 60 min).

spontaneous precipitation depended on the initial pH of FPW (pH 11), BPW (pH 1.5) and dissolved cupric salt at room temperature. In order to determine whether temperature was the limiting factor, a series of designed experiment were carried out at different temperatures. The temperatures were tested in the interval of 423–523 K while the rest of the parameters were kept at the same condition (initial O₂ partial pressure was tested at 1.4 MPa and 60 min reaction time). As for the temperature series, some appreciable influence was noticed when temperature was changed strikingly. As observed in Fig. 1, in the range of 423–523 K, removal efficiency of COD and TOC achieved roughly 41% and 43% respectively at 523 K. Moreover, this parameter decreased by down to ca. 27% and 31% at 423 K, implying that higher temperature matters has a significant impact on the removal of COD and TOC.

Additionally, three different samples with initial oxygen partial pressure of 0 MPa, 0.7 MPa, and 1.4 MPa at the reference temperature of 523 K, were tested to study the effect of oxygen partial pressure on the performance of the CWAO process. As illustrated in Fig. 2, the stoichiometry amount was defined as the amount of oxygen needed to chemically mineralize all the pollutants in the mixture. A COD reduction of ca. 10% and a TOC removal of 10% could be achieved by simple thermal decomposition before zero reaction time (during the process of heating), the reduction of COD and TOC is more excellent at 1.4 MPa than that of under lower pressure

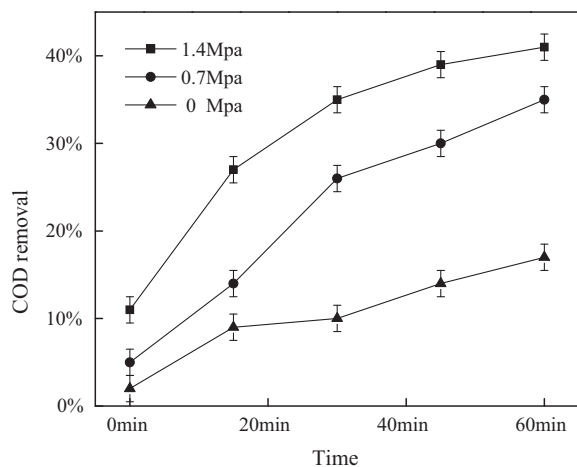


Fig. 2. Effect of oxygen initial pressure on COD removal at 523 K (initial O₂ pressure: 0, 0.7, 1.4 MPa; reaction time: 60 min).

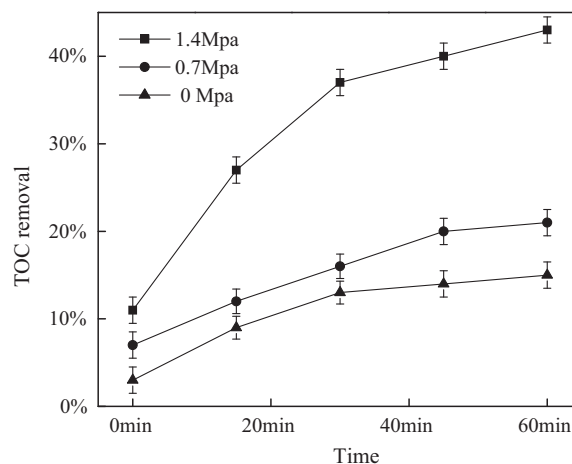
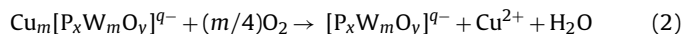


Fig. 3. Effect of oxygen initial pressure on TOC removal at 523 K (initial O₂ pressure: 0, 0.7, 1.4 MPa; reaction time: 60 min).

conditions. Figs. 2 and 3 showed that a significant increase in both COD and TOC removal was observed at an initial oxygen pressure of 1.4 MPa, the COD and TOC removal rates were found to come up with initial pressure increased. Incidentally, we noted that the COD removal exceeded the oxygen supplied at low oxygen partial pressure. For example, 41% of COD removal was achieved with only 15% of oxygen supplied. The reason for this phenomenon was that the removal of COD was the overall result of oxidation reaction and thermolysis.

A survey of CWAO catalysts showed that the wet oxidation reaction proceeds via a free-radical mechanism [21]. However, the state of POM in the solution is generally complicated by a series of pH-dependent equilibrium, involving a variety of factors. These equilibria, with a few exceptions, were largely unknown. As a result, relatively little exact knowledge of mechanisms of POM catalyzed oxidation was available [18]. It was deduced that mechanisms of wet oxidation in autoclave by Cu²⁺[P_xW_mO_y]^{q-} co-catalyst proceed similarly with the relative mature theories of HPA, also via a stepwise redox mechanism represented by (Eqs. (1) and (2)) as following:



The thermodynamic condition for the occurrence of reactions can be approximately represented the redox potentials of the organics, with POM and O₂ [22,23],

$$E(\text{red}) \leq E(\text{HPA}-n) \leq E(\text{O}_2) = 1.23\text{V} \quad (3)$$

The redox potential $E(\text{POM})$ should be higher in comparison with $E(\text{HPA}-n)$ 0.7V (Eq. (3)) [24]. Hence the high temperature and co-catalyst fulfills for a wide variety of COD as reductant degradation.

3.2. Products of wet air oxidation and biodegradability studies

Knowledge of the chemical composition of CWAO effluent is essential in determining the effectiveness of the CWAO system and selecting further treatment [25]. In particular, short organic acids such as acetic acid or propionic acid can accumulate in wet air oxidation effluents. These short-chain molecules tend to be resistant to further oxidation but would be ideal for biological treatment [26]. As Fig. 4 depicted, retention time and component percentage of the gas chromatography data file for effluent were simplified, and a series of volatile organics peaks were observed at different

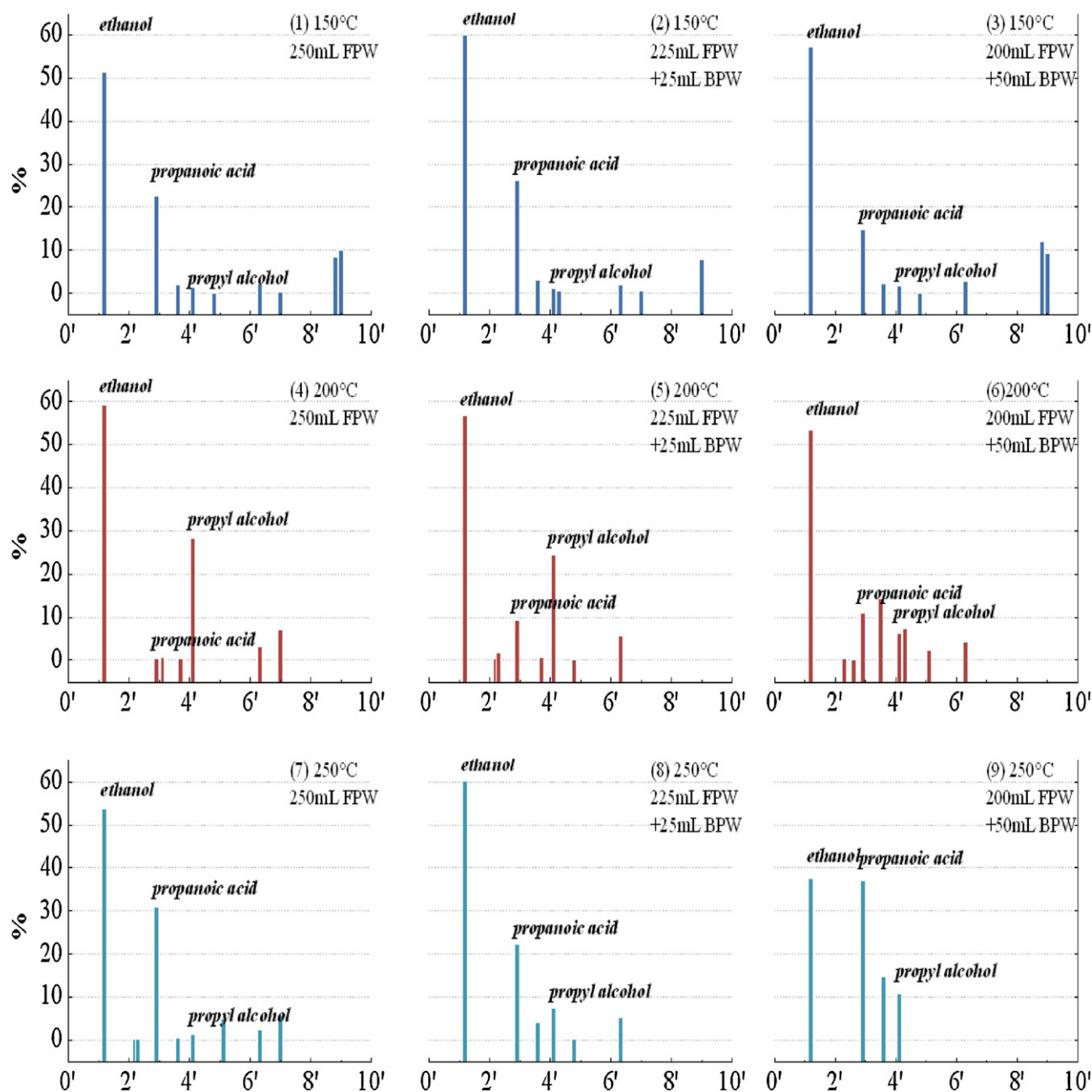


Fig. 4. Typical gas chromatograms of volatile products from CWAO effluent liquid sample.

retention times. Analysis of the effluent products has been reported for the different volume ratios of FPW:BPW at temperature range of 423–523 K over the same oxygen initial pressure 1.4 MPa. In the presence of superfluous alcohol containing in FPW, intermediate products of CWAO were found, including propionic acid at ca. 2.9 min, propyl alcohol at ca. 4.1 min, and some other unknown components. Moreover, Acetic acid as specific biodegradable product in many previous studies, were not found. Fig. 4(1)–(3) showed the tendency of product distribution at 423 K, the last retention time of volatile matter was detected near 9 min, implying that incomplete oxidation at 423 K tend to produced macromolecule which was identified as secondary pollution. With increasing temperature to 473 K, macromolecule was found vanished at 9 min as illustrated in Fig. 4(4)–(6). Finally, biodegradable products such as propanoic acid, propyl alcohol etc. were produced in the CWAO period.

On the other hand, following the FPW:BPW volume ratio range from 250 mL:0–200 mL:50 mL, we observed that yield of propanoic acid increased by 10% (volume fraction), it can be deduced that adequate Cu^{2+} dissolved in 50 mL berberine wastewater combined with PO_4^{3-} , WO_3^- generated following CWAO reaction of fosfomycin wastewater to form an interactive polyoxometalate co-catalyst system which kept inconspicuous in the whole CWAO process as an effective catalysis. The phenomenon of (7)–(9) confirms the preceding statement that the temperature and FPW:BPW volume ratio should be two key factors for the further biodegradation. Meanwhile, the BOD_5 of CWAO effluent samples were investigated in Table 3. To some extent, BOD_5/COD was enhanced under different CWAO conditions, BOD_5/COD elevated in a narrow range with FPW:BPW=225 mL:25 mL at 473 K, 1.4 MPa. Moreover, The BOD_5/COD of influent ascended from nonexistent to 0.41 of effluent, reached maximum at 523 K,

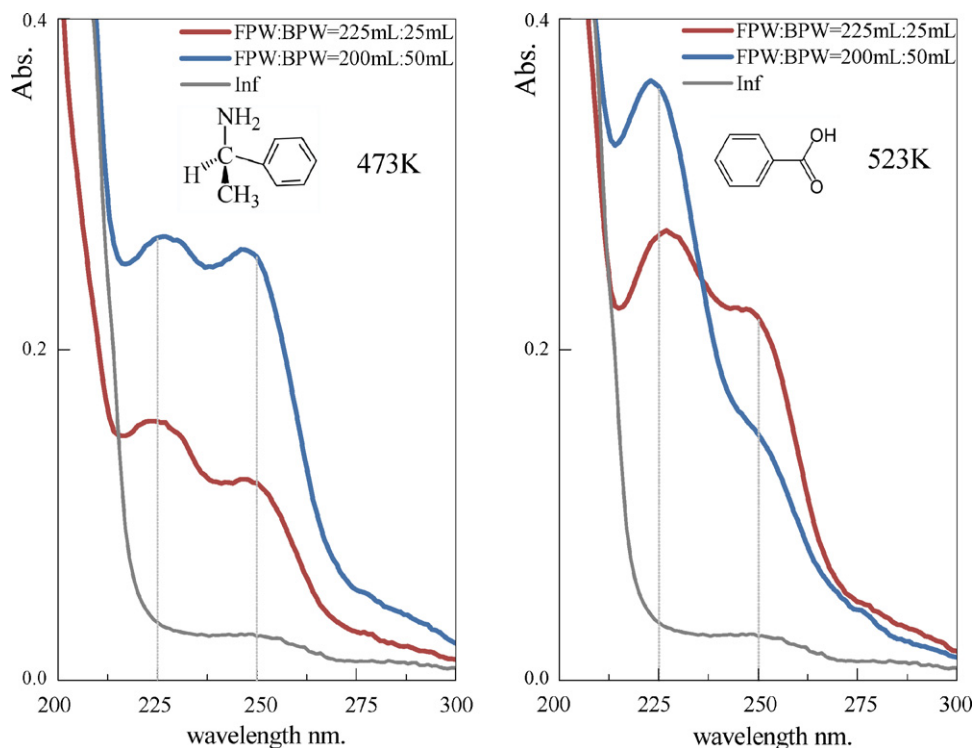


Fig. 5. The UV-vis spectrum absorption of effluent samples under different conditions. Absorption value increasing depends on the volume of BPW, 50 mL BPW render absorption value of 225 nm reach near 0.25 at 473 K and 0.35 at 523 K, respectively.

1.4 MPa, FPW:BPW = 200 mL:50 mL, suggesting that the CWAO effluent was suitable to successive biological treatment. It is worth noting that BOD₅/COD had not achieved optimal ratio, which value was in range of 0.5–0.75 approximating to domestic sewage according to previous research [26]. In order to clarify that which intermediate product was more resistant to biodegradation, UV-vis spectroscopy of effluent samples was analyzed as Fig. 5 depicted. Before treatment, the UV-vis spectra of influent had barely detectable absorption bands in the near-ultraviolet region (225–350 nm). Moreover, biotoxic substrate from influent such as considerable amount of alcohol, which exhibits very strong absorption near 200 nm, caused samples non-biodegradable or toxic, and influent BOD₅ showed nonexistent in Table 3 especially. As illustrated in Fig. 5, the CWAO effluent (473 K) had two almost the same strength absorption at 225 nm ethylene band (E2 absorption band) and 250 nm benzene band (R absorption band) in polar solvent (dilute samples in deionized water). The possible reason for this phenomenon was that 250 nm peak resulting from $n \rightarrow \pi^*$ transitions were shifted to shorter wavelengths (blue shift) with increasing solvent polarity, this peak arises from increased solvation of the lone pair, which lowers the energy of the n orbital, so the reverse (i.e., 225 nm peak red shift) was seen for $\pi \rightarrow \pi^*$ transitions. Supposedly, these two UV bands were characteristic of intermediate products for phenylethylamine [27], which contained conjugated double bonds (at 225 nm and 250 nm) were known to be

harmful to aquatic life in very low concentrations. As temperature increase to 523 K, the intensity of absorption at 250 nm declines extremely obvious, it suggests that effluent intermediate product evolved out of phenylethylamine, whereas the 225 nm conjugated absorption band was characteristic of benzoate in the mixture of water and alcohol [28,29], these results obtained confirmed that the CWAO process had a significant effect on the oxidative degradation of organic matter for BOD₅/COD enhancement at 523 K, although these oxidation product showed a little toxic to microbes.

3.3. Properties of POM catalyst

In order to get insight to this polymetalate catalyst, the supernatant of CWAO effluent was skimmed after reaction, and a large amount of precipitated crystal contained Cu²⁺ and [P_xW_mO_y]^{q-} polyoxometalate can be easily obtained at the bottom of

Table 3
The degradation of effluent sample under different CWAO reaction conditions.

Condition	FPW:BPW volume ratio	Eff COD (mg/L)	Eff BOD ₅ (mg/L)	BOD ₅ /COD ratio
473 K, 1.4 MPa	225 mL:25 mL	87,294	12,221	0.14
	200 mL:50 mL	81,730	11,442	0.14
523 K, 1.4 MPa	225 mL:25 mL	79,640	26,281	0.33
	200 mL:50 mL	71,353	29,255	0.41

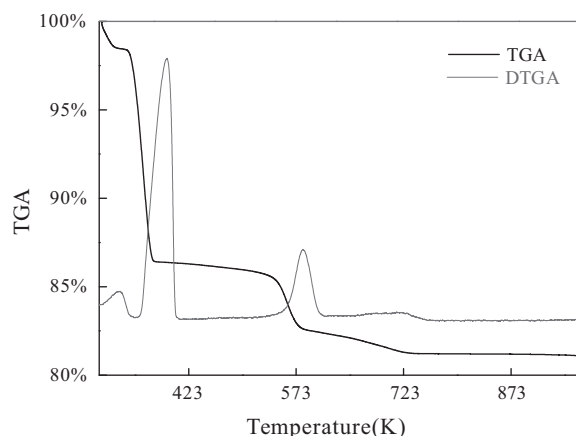


Fig. 6. TGA plots for POM precipitated crystal from CWAO effluent.

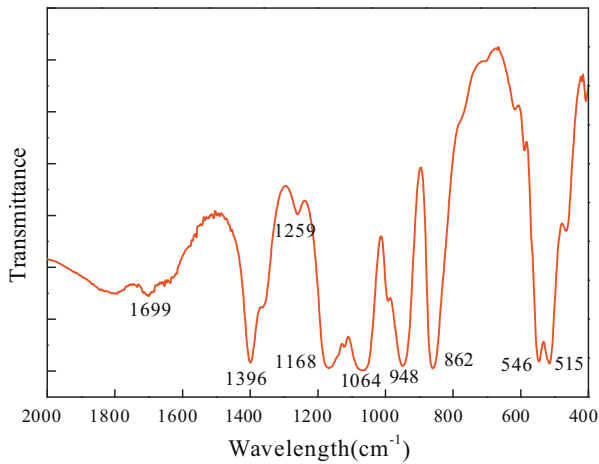


Fig. 7. FT-IR spectra (KBr) of crystallized products in CWAQ effluent.

effluent storage box. The thermal stability of the precipitated crystal from CWAQ effluent was represented in Fig. 6, the first weight loss before 400 K was 14% and could be attributed to elimination of adsorbed water molecules. Moreover, the significant thermal stable state was observed at the range of 423–540 K without weight loss, and this character could meet the requirement of conventional CWAQ temperature condition, which was generally set at the range of 423–573 K. The IR spectrum (Fig. 7) of precipitated crystal gave the four characteristic peaks at 1170, 1070, 950, 860 cm^{-1} , which were attributed to the asymmetry vibrations P–O in polyoxometalate [8], in addition, a strong adsorption peaks were obtained at 1396, 1699 cm^{-1} in agreement with previously published propionic specific peaks [30]. Obviously, this result consistent with the afore-said analysis of CWAQ product. The precipitated crystal belonged to lacunary polyanions series compared with so-called intact Keggin or Dawson structure [31]. It could be deduced that the crystallization of specific substituted positional isomers of these species had been doped because of uncertain or tanglesome reaction mechanism, especially in CWAQ process of real wastewater treatment. The unknown content of major or minor elements was determined as Fig. 8 showed, the XRF measurements confirmed that high P,

Table 4
Elemental composition of precipitate from CWAQ influent.

CuO	P ₂ O ₅	Cl	WO ₃	Na ₂ O	CaO
32.3%	23.4%	17.4%	12.9%	12.2%	0.524%
SO ₃	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MoO ₃	BaO
0.29%	0.295%	0.215%	0.199%	0.137%	0.112%
Compton	Rayleigh	Sum			
0.74	1.01	100.00%			

W and Cu amounts were to be found in precipitated crystal in Table 4, which were loaded with about 32.3 wt.% CuO, 23.4 wt.% P₂O₅, and 12.9 wt.% WO₃. Though relatively efficient, the method of recycling polyoxometalates by precipitation with polyanions was also rather incomplete, in this work, CuO, P₂O₅ and WO₃ were not completely removed from CWAQ effluent. To identify the structure of the precipitated crystal, XRD spectroscopy was performed and result was given in Fig. 9, the pattern of the precipitated crystal showed that characteristic peaks at $2\theta = 10.3^\circ, 16.6^\circ, 24.1^\circ, 26.4^\circ$

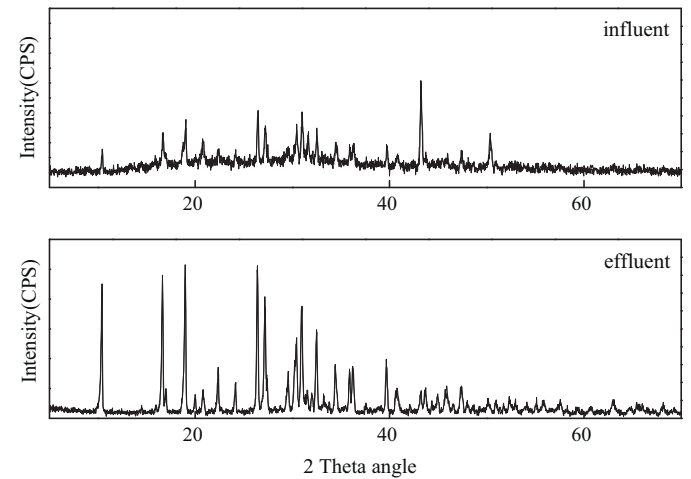


Fig. 9. XRD patterns of precipitated crystal from influent and effluent respectively XRD analyses conditions; start: 5°; end: 70°; step: 0.01°; step time: 1 s; temp: 25 °C (room).

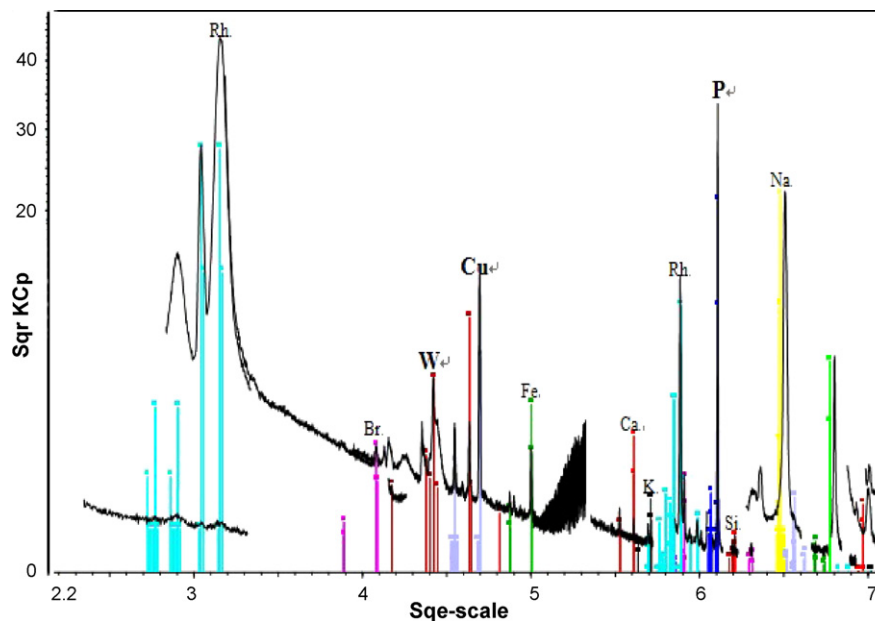


Fig. 8. XRF pattern of precipitated crystal from effluent.

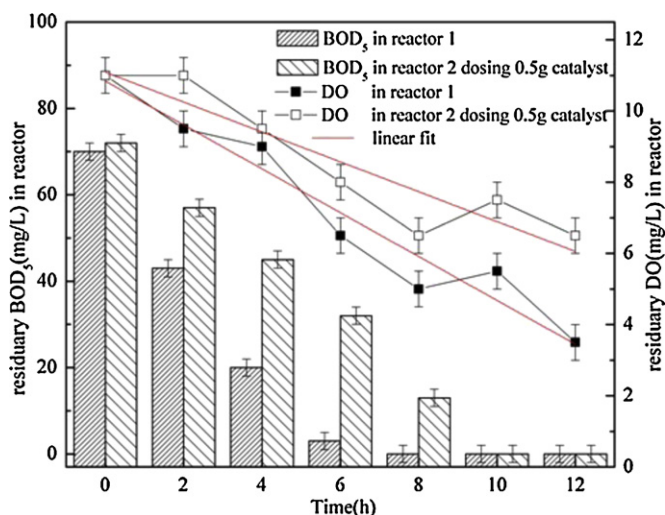


Fig. 10. The effect of catalyst toxicity on BOD₅ and dissolved oxygen utilization of microorganism.

were similar to the reference pattern of P₄W₈O₃₂ phase (JCPDS No. 75-2248). Obviously, it showed that the composition of influent or effluent, temperature, and recrystallization could disturb co-catalyst crystallization, and leading to form lacunary polyanions series as mentioned previously. XRD result also confirmed that the intensity of crystal precipitated in effluent was stronger than those from influent, the reason for this phenomenon was that during temperature rise back to lower temperature period, the co-catalyst components was forced to restructure for recrystallization, meanwhile macromolecule or intricate organics, which would obstruct the crystallization of Cu²⁺ and [P_xW_mO_y]^{q-} co-catalyst system, was decomposed by wet air oxidation with aforesaid catalyst system. Furthermore, a series of contrast test were conducted to evaluate the biological toxicity of Cu²⁺ and [P_xW_mO_y]^{q-} co-catalyst in two 1L enclosed reactors. 1# reactor was fed with synthetic wastewater which has a BOD₅ value of 75 mg/L as well as 2# reactor, but 1 g catalyst was dosed into reactor 2 at the beginning of experiment. Constantly mixing conditions were kept the same for both reactors during 12 h test time. In experiments designed to observe effects of catalyst inhibition or toxicity on active sludge, BOD₅ and dissolved oxygen were studied as Fig. 10 showed. Bacterial metabolism result in dissolved oxygen decreasing in both reactor with linear fitting method (straight line in Fig. 10), oxygen uptake rate (OUR) was calculated to be 0.62 in 1# reactor compare with 0.42 in 2# reactor. This suggested that catalyst presence in 2# reactor could affect microorganism in employing oxygen. In addition, BOD₅ removal efficiency in 2# reactor was reduced. After 6 h reaction time, residuary BOD₅ of 32 mg/L in 2# reactor was unemployed, meanwhile, initial BOD₅ of 75 mg/L in 1# reactor was almost removed. In general, presence of catalyst in high concentrations (1 g/L) showed slightly harmful to aquatic microorganism, it is a reasonable consideration that Cu²⁺ component of catalyst would play a vital role in employing DO and BOD₅. These are consistent with other research showing that addition of Cu²⁺ to a laboratory activated sludge system caused a 75% reduction in substrate conversion and oxygen utilization [32]. However, Cu²⁺ and [P_xW_mO_y]^{q-} co-catalyst showed harmfulness compared with previous research, the reason may be that the catalyst precipitated out as solids, and the dissociation of Cu²⁺ could not be easily completed.

4. Conclusion

CWAO by Cu²⁺ and [P_xW_mO_y]^{q-} co-catalysis was found to be an effective method for treating the real pharmaceutical

wastewater discharged from fosfomycin and berberine manufacturing shop. More than 40% COD reduction and TOC removal could be realized under proper operating reaction conditions and FPW:BPW volume ratio. Increasing the reaction temperature and pressure helped to enhance the CWAO efficiency. However, satisfactory ratio of BOD₅/COD had not been achieved for further biodegradation due to the toxicity of complex products. The use of Cu²⁺ and [P_xW_mO_y]^{q-} co-catalysis in these processes would vastly simplify catalyst removal in aspect of solid liquid separation, minimize the amount of waste formed. The characteristics of Cu²⁺ and [P_xW_mO_y]^{q-} co-catalysis showed that it was not in agreement with Keggin or Dawson structure but a type of lacunary polyoxometalate formed mostly depends on FPW:BPW volume ratio.

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