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Advanced treatment of paper mill wastewater by catalytic vacuum distillation

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ABSTRACT

A new economical, environmentally friendly wastewater treatment method, catalytic vacuum distillation (CVD) advanced wastewater treatment, is introduced in this paper. The CVD degradation of pulp and paper mill wastewater assisted by some promoters, such as sodium hydrate, ferric chloride and kaolin was investigated. The results show that the initial pH plays an important role on the chemical oxygen demand (COD) reduction and color removal. Kaolin can improve slightly the effect of treatment by vacuum distillation. Moreover, no distinct improvement effect was observed when ferric chloride was introduced into the catalytic vacuum distillation system. The results show that the quality of some effluents can reach the standard of discharged wastewater. In addition, manifested by the effects of this method, the vacuum distillation is a promising technique for wastewater treatment.

Keywords: Vacuum distillation; Advanced treatment; Paper mill wastewater

1. Introduction

Up to now, paper industry is one of the most industrial pollution sources in the world, which consumes over 60 m^3 of wastewater per ton of paper produced, resulting in large amounts of wastewater generation and concomitant economic and ecological/ environmental costs/ problems [1]. Indeed, such wastewater contains a large amount of pollutants characterized by biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), toxicity, and colorants which cause bacterial and algal slime growth, thermal impacts, scum formation, color problems, and a loss of both biodiversity and aesthetic beauty in the environment [2]. Therefore, paper mill wastewater is difficult to be treated. In particular, a lot of small paper mill have been closed in Shaanxi Province, China since 2000, as their effluents can not meet the legal restrictions that require high quality for effluent before discharged into the environment (COD < 100 mg L^{-1} for effluent discharge standard, COD removal efficiency is more than 97.3%).

The main common treatment processes used in pulp and paper mill plants are primary clarification (sedimentation or flotation), secondary treatment (activated sludge process or anaerobic digestion) and/or tertiary processes (membrane processes as ultrafiltration) [3]. Activated sludge plants are the most common wastewater treatment process for the removal of organics in our country; however, there are several problems with the process: it produces sludges with very variable settlement properties, it is sensitive to shock loading and toxicity, and its capacity to remove poorly biodegradable toxic substances is limited. Therefore, many researchers attempted to develop a new technology for complementing or even replace some of these treatments. For several decades, a number of methods have been developed, such as adsorption-separation [4, 5], electrocoagulation [6], chemical oxidation [7],

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wet oxidation (WO) [8, 9] and catalytic wet air oxidation [10]. Although wet air oxidation has been found to reduce COD in a large extent in these methods, the high energy consumption and the use of high-pressure reactors make the wet air oxidation for large amount of wastewater uneconomical and unviable [11].

However, without disregarding the already summarized treatment techniques, one of the most interesting and effective process for treating some pollutants in wastewater is the distillation process, because of its convenience and typically higher efficiency than the above traditional methods [12, 13]. Furthermore, distillation process also has been used commercially in the production of diacetone alcohol [14], and methyl tert-butyl ether [15] with some catalysts (also called catalytic distillation (CD) process). In addition, distillation technique also can be applied in seawater desalting [16–18]. However, an important characteristics of industry effluents which themselves often have a lot of thermal energy with moderate high temperature (for example, temperature of 50°C paper mill effluents) is neglected during conventional effluent disposal. So in our study, a combined technology, catalytic vacuum distillation (CVD), that a vacuum pump added in the distillation system and assisted with some promoters, is proposed for the treatment of wastewater with residual heat of effluents. During this process, much costly energy can be saving, meanwhile, the heat released by catalytic reaction can be also efficiently used by distillation to generate more vapors.

Here, the vacuum distillation process was used to treat paper mill wastewater after sedimentation which achieved a high removal of suspended solids. The experiments were carried out at different pH assisted with different promoters (NaOH, H_2SO_4, $FeCl_3$ or kaolin), to ascertain the feasibility of vacuum distillation process in paper mill wastewater treatment. The optimal operation condition was investigated by comparison the activity of various promoters. The major target parameter of COD index was assessed so as to characterize the performance of the different CVD systems.

2. Experimental details

2.1. Reagents and materials

The chemical reagents used and kaolin (surface area: 20 $m^2\ g^{-1}$ and pore volume: 0.5 $cm^3\ g^{-1}$) are of analytical grade without further purification.

The wastewater used in this research was supplied by a paper mill near Xi'An, obtained from the equalization tank in the wastewater treatment plant, and its characteristics are listed in Table 1. Before the experiment the wastewater used was treated by primary clarification (sedimentation) first, and then was treated by distillation process.

Table 1
Characteristic of the pulp and paper mill wastewater.

Characteristics	Value
pH	13.48±0.02
COD (mg L^{-1})	3650.00±0.50
BOD (mg L^{-1})	870.00±0.05
Total solids (mg L^{-1})	1550.0±0.1
Suspended solids (mg L^{-1})	340.0±0.1
Dissolved solids (mg L^{-1})	1210.0±0.1

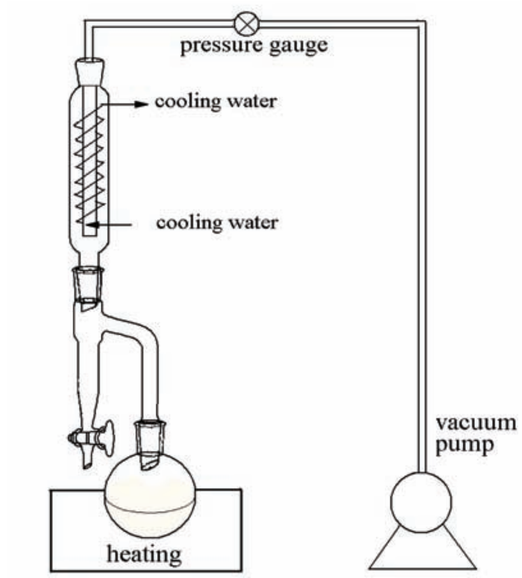

Fig. 1. Experimental set-up used in the laboratory-scale study.

2.2. Experimental process

The characteristics of the vapour–liquid equilibrium were evaluated in the laboratory scale represented in Fig. 1. This equipment consisted of a round-bottomed flask connected to a water-cooled condenser and a Dean–Stark apparatus to collect distilled samples. Samples were heated by means of a constant temperature water bath apparatus. A vacuum pump was also fitted to enable operations in the pressure range between atmospheric pressure and 4 kPa (a vacuum pressure gauge was used to measure the operating pressure). For each run, 150 mL of raw wastewaters was filled into the flask, and then the promoters were added into wastewater. Subsequently, the continuous operation of vacuum distillation was begun and the condensate was drawn at regular intervals and analyzed by COD and ultraviolet absorption methods during each experiment so as to evaluate the efficiency of different CVD processes for wastewater treatment.

Operating conditions: water was distilled at 43 ± 2°C when vacuum degree was 93 ±1 kPa. This temperature accorded with practical situation of discharged paper mill wastewater. Thus, this method was economical in energy, only needs negative pressure by vacuum-pumping.

2.3. Analytical method

The COD was chosen as the parameter to evaluate the quality of treated water, which was determined according to standard methods [19, 20]. The pH of the solution was measured using an Orion 290 pH meter. The UV–vis (UV-7504, China) spectrum of the sample was recorded. The maximum visible absorbance wavelength was detected. The color removal ratio was calculated as follows:

$$\text{decolorization (\%)} = \frac{ABS_0 - ABS}{ABS} \times 100\%$$

ABS_0 and ABS are the absorbance values before and after vacuum distillation, respectively.

3. Results and discussion

3.1. Effect of initial pH

Generally, paper mill wastewater mainly contains two kinds of organic compounds, phenol and lignin-derived so that it has high COD. At first, in order to investigate the volatility of volatile components in wastewater, raw wastewater was treated by vacuum distillation at different initial pH and the results are shown in Fig. 2. As can be seen from this figure, the COD value of condensate distilled directly from raw wastewater (pH =13.5, COD: 3650 mg L^{-1}) are 102.07 and 69.87 mg L^{-1} for 20 and 40 min, respectively, which suggests that the vacuum distillation is an effective technique for wastewater treatment. On the other hand, considering the influence of pH values, the pH of wastewater was adjusted over 14 with 8% sodium hydrate, followed by the same method mentioned above so as to obtain the improved effect of COD. 20 min later the COD value decresed to 95.44 mg L^{-1}, which is better than that of raw samples. However, with the treated time prolonging, the COD reduction has a little change and it was slightly lower than that of the distillation without sodium hydrate. Furthermore, when the pH of paper mill wastewater was adjusted to 7, 3 and less than 1 with 1 M sulphuric acid, respectively, the COD value all increased than that of alkaline condition treated with 40 min, indicating that the high alkaline condition is in favor of the COD removal efficiency.

Comparing with the above experimental results, it can be found that the initial pH play an important role in the wastewater treatment. At the beginning 20 min, a high COD reduction for wastewater of 97.4% can be reached with 8% sodium hydrate added (pH > 14). However, with the treated time prolonging, the COD removal of wastewater almost unchanged (97.9% at 40 min). In general, the COD reduction efficiency in alkaline condition is better than that of in acidic condition, but the high alkalinity is not always a good thing in COD removal. The possible reason can be interpreted as follows: phenol is a kind of volatile organic compounds, it can be transformed to phenolate in alkaline condition (Eqs.1–2):

$$C_6H_5 - OH + OH^- \rightarrow C_6H_5 - O^- + H_2O \quad (1)$$

$$C_6H_5 - O^- + Na^+ \rightarrow C_6H_5 - ONa \quad (2)$$

So its volatility reduced and high COD reduction for wastewater can be observed. As another main component in paper mill wastewater, lignin is a three-dimensional polyphenolic macromolecule with complex structure [21], constituted by phenyl propane, phenolic hydroxyl groups, methoxyl and aryl-ether [22], a general formula was R—OH. At cooking process, the ether bond was broken because of the role of caustic soda, and lignin macromolecules gradually degraded into the form of alkali lignin, which was hydrophilic and soluble in black liquor completely. The electrophilic substitution reaction

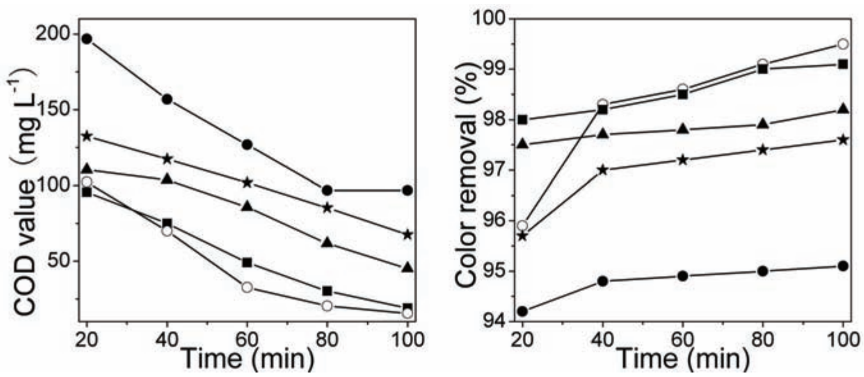

Fig. 2. Effect of initial pH on COD value and color removal (○ pH = 13.5, ■ pH > 14, ▲ pH = 7, ● pH = 3, ★ pH < 1).

was occurred when black liquor was neutralized by acid, so that the colloidal alkali lignin was destructed to insoluble lignin in water, which then separated from the black liquor.

$$2R - ONa + H_2SO_4 \rightarrow 2ROH \downarrow + Na_2SO_4 \quad (3)$$

So lignin was precipitated in proper pH values [21, 23], which decrease the COD in wastewater and then reach the standard of discharged, though the effect was a little poorer at pH of 3 than that of in alkaline condition.

The trend of color removal with reaction time is also shown in Fig. 2. The color removal of raw wastewater are close to 99% at the end of 100 min, and >97% decoloration can be obtained for neutral and alkaline condition at 20 min, while the lowest decolorization was obtained in pH = 3, indicating that the pollutants with color was almost removed from the wastewater, and better decoloration can be achieved in neutral and alkaline condition.

3.2. *Effect of kaolin*

Kaolin is a common natural clay with ionic crystalline structure, and excellent adsorption properties for some organic molecules with opposite ionic character [24]. As one of the clay materials, kaolin is most widely used in many fields, such as ceramics, paper coating, paper filling, paint extender, rubber filler, plastic filler, cracking catalysts, or cements [25,26]. However, little attention has been paid on kaolin's application in wastewater treatment [27–29].

To evaluate the effect of kaolin in vacuum distillation process, 1.6% kaolin was added into raw wastewater with or without 8% sodium hydrate, respectively, which were then treated by vacuum distillation, expecting kaolin can decrease the volatility of organic compounds due to its special adsorption property. The COD value and color removal as a function of time are presented in Fig. 3. As can be seen from the figure, the changes of COD value and color removal with kaolin are almost the same as that of the raw wastewater without kaolin in 20 min, but a little better efficiency can be observed in 40–100 min with continuous changes, indicating that the adsorption capacity of kaolin can improve the COD reduction efficiency and color removal. However, the COD reduction efficiency of wastewater with 8% sodium hydrate and kaolin is lower than that of only 8% sodium hydrate used, and the color removal is the same result, indicating that the introduction of kaolin into the wastewater with 8% sodium hydrate cannot improve the COD reduction and the color removal efficiency. Due to the COD value of wastewater with sodium hydrate and kaolin is higher than that of only kaolin used, it can be concluded that no synergetic effect exists between sodium hydrate and kaolin in this CVD system. It is probably because that the kaolin particle acquires a negative surface charge at that pH [30] which reduced the adsorption capacity of kaolin comparing with the raw wastewater.

3.3. *Effect of ferric chloride*

In order to improve the treatment effect in neutral and acidic conditions, ferric chloride has been introduced into the CVD process of wastewater treatment. As a good coagulation, ferric chloride has been widely applied in wastewater treatment. The reason for this is that ferric chloride solution can hydrolyze to form $Fe(OH)_3$ gel when heated, and the flocs had large surface area that is beneficial for rapid adsorption of soluble organic compounds and trapping of colloidal particles [31].

When the pH of paper mill wastewater was adjusted with 1 M sulphuric acid to 7, 3 and less than 1, respectively, ferric chloride (0.03 mol L^{-1}) was added in the wastewater. The COD value and color removal at different pH in the same reactor with and without ferric chloride were compared and the results are shown in Fig. 4.

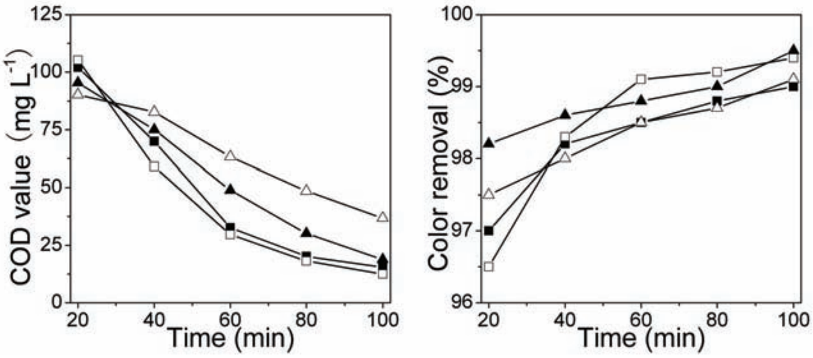

Fig. 3. Effect of kaolin on COD value and color removal efficiency (■ raw wastewater, □ wastewater with kaolin, ▲ wastewater with NaOH, △ wastewater with kaolin+NaOH).

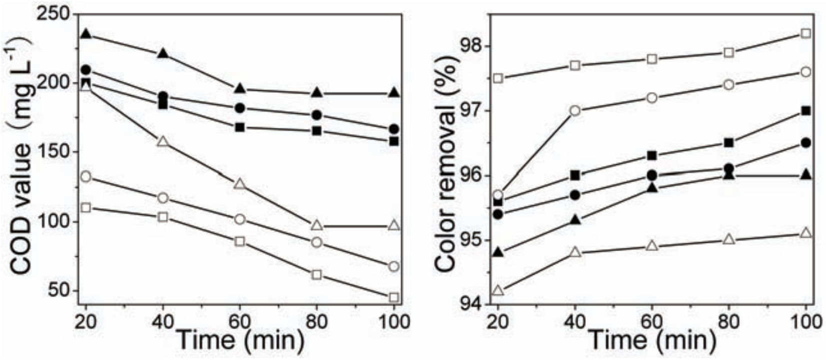

Fig. 4. Effect of ferric chloride at different pH on COD value and color removal efficiency (■□ pH = 7, ○● pH = 3, ▲△ pH < 1, hollow: without ferric chloride; solid: with ferric chloride).

Table 2
The efficiency of CVD assisted with different promoters on COD reduction.

Treatment	20 min	40 min	60 min	80 min	100 min
Raw wastewater	97.20%	98.09%	99.11%	99.45%	99.58%
with Kaolin	97.12%	98.38%	99.19%	99.50%	99.66%
pH > 14	97.38%	97.94%	98.66%	99.17%	99.48%
kaolin + NaOH	97.53%	97.73%	98.27%	98.67%	98.99%
pH = 7	96.98%	97.16%	97.65%	98.31%	98.77%
pH = 3	96.37%	96.79%	97.21%	97.67%	98.15%
pH < 1	94.61%	95.70%	96.53%	97.35%	97.35%
$FeCl_3$ (pH = 7)	94.51%	94.95%	95.40%	95.47%	95.68%
$FeCl_3$ (pH = 3)	94.26%	94.78%	95.02%	95.16%	95.43%
$FeCl_3$ (pH < 1)	93.56%	93.95%	94.65%	94.73%	94.73%

Higher COD value were obtained in CVD system with the introduction of ferric chloride at all acidic conditions, and the highest COD value was observed for pH < 1. The color removal efficiency at pH of 7 and 3 almost have the same trend: lower decoloration were obtained in the system assisted with ferric chloride, however at pH < 1, the color removal is improved by the addition of ferric chloride. All the results suggest that no significant improvement can be observed when ferric chloride has been introduced into catalytic vacuum distillation system.

Table 2 summarize the detailed results about the influence of the CVD assisted with different promoters on the COD reduction for paper mill wastewater. From the table, it can be found that high COD reduction (>93%) can be obtained in all CVD system, indicating that CVD is an appropriate and effective method for treating paper mill wastewater. Moreover, increasing alkalinity can improve the treatment efficiency, maybe due to the high volitality of phenol has been transformed phenolated in alkaline conditions. The optimal COD reduction (99.66%) can be achieved when raw wastewater treated with CVD system assisted with kaolin for 100 min. The condensate from these processes can be reused or discharged when treated by the tertiary processes (membrane processes as ultrafiltration).

4. Conclusion

CVD system assisted with different promoters, such as sodium hydrate, ferric chloride and kaolin were applied in paper mill wastewater in lab-plant. The effect of different promoters has been investigated and satisfied results have been obtained. For the raw wastewater (pH 13.5) in the presence of kaolin treated by vacuum distillation, the highest COD reduction and color removal efficiency of 99.66% and 99.2% in 100 min were obtained. From the experimental results, it can be concluded that vacuum distillation is advantageous to purify the paper mill wastewater. More importantly, no additional contaminants produced in all distillation processes, so vacuum distillation advanced wastewater technology is an environmentally friendly wastewater treatment method.

References

[1] G. Thompson, J. Swain, M. Kay, C.F. Forster, Bioresour. Technol., 77 (2001) 275–286.
[2] D. Pokhrel, T. Viraraghavan, Sci. Total Environ., 333 (2004) 37–58.
[3] G. Thomson, J. Swain, M. Kay, C.F. Forster, Bioresour. Technol., 77 (2001) 275–286.
[4] A.R. Shawwa, D.W. Smith, D.C. Sego, Water Res., 35 (2002) 745–749.
[5] R.M. Narbaitz, R.L. Droste, L. Fermandes, K.J. Kennady, D. Ball, Water Sci. Technol., 35 (1997) 277–282.
[6] M. Ugurlu, A. Gurses, C. Dogar, M. Yalcm, J. Environ. Manage., 87 (2008) 420–428.
[7] Y. Wang, B. Wang, H.Z. Ma, J. Hazard. Mater., B137 (2006) 1853–1858.
[8] D.B. Akolekar, S.K. Bhargava, I.S. Shirgonkar, J. Prasad, Appl. Catal. A: Gen., 236 (2002) 255–262.
[9] S. Verenich, A. Laari, J. Kallas, Waste. Manage., 20 (2000) 287–293.
[10]A. Pintar, M. Besson, P. Gallezot, Appl. Catal B: Environ., 31 (2001) 275–290.
[11] Q. Zhang, K.T. Chuang, Adv. Environ. Res., 3 (2001) 251–258.
[12] G. Gutiérrez, J.M. Bentito, J. Coca, C. Pazos, Ind. Eng. Chem. Res., 48 (2009) 2100–2106.
[13] J.M. Benito, G. Ríos, E. Ortea, *et al*. Desalination, 147 (2002) 5–10.
[14] G.G. Podrebarac, F.T.T. Ng, G.L. Rempel, Chem. Eng. Sci., 53 (1998) 1067–1075.
[15] J. Wang, Y. Chang, E.Q. Wang, C.Y. Li, Com. Chem. Eng., 32 (2008) 1316–1324.
[16] M. Reali, Desalination, 190 (2006) 29–42.
[17] M. Reali, Desalination, 207 (2007) 304–323.
[18] M. Reali, Desalination, 212 (2007) 219–237.
[19] S.P. Faulkner Jr., W.H. Patrick, R.P. Gambrell, Soil Sci. Soc. Am. J., 53 (1989) 883.
[20] American Public Health Association, American Water Works Association and Water Pollution Control Federation, Standard Methods for the Examination of Water and Wastewater, 19th edn, American Public Health Association, Washington, DC, 1995.
[21] S.I. Mussatto, M. Femandes, I.C. Poberto, Carbohyd. Polym., 70 (2007) 218–223.
[22] Ángel T. Martínez, Jorge Rencoret, Gisela Marques, *et al*. Phytochemistry, 69 (2008) 2831–2834.
[23] C. Vila, V. Santos, J.C. ParajÓ, Bioresource Technol., 90 (2003) 339–344.
[24] B.K. Nandi, A. Goswami, M.K. Purkait, J. Hazard. Mater., 161 (2009) 387–395.
[25] W.M. Bundy, *Kaolin genesis and utilization*, H. Murray, W. Bundy, C. Harvey, (eds), Special Publication No. 1; The Clay Minerals Society, Boulder, CO, 1993, 43.
[26] H.H. Murray, Appl. Clay Sci., 17 (2007) 207–221.
[27] B. Wang, L. Gu, H.Zh. Ma, J. Hazard. Mater., 143 (2007) 198–205.
[28] H.Zh. Ma, B. Wang, Y. Wang. J. Hazard. Mater., 145 (2007) 417–423.
[29] Q.F. Zhuo, H.Zh. Ma, B. Wang, L. Gu. J. Hazard. Mater., 142 (2007) 81–87.
[30] B.K. Nandi, A. Goswami, M.K. Purkait, J. Hazard. Mater., 161 (2009) 387–395.
[31] Y.H. Shi, M.H. Fan, R.C. Brown, S. Sung, J.V. Leeuwen, Chem. Eng. Process., 43 (2004) 955–964.