Treatment of petroleum refinery wastewater by distillation-assisted catalytic oxidation under low temperature and low pressure

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ABSTRACT

A distillation-assisted catalytic oxidation (DACO) process under low temperature (100°C) and atmospheric pressure was investigated to treat heavily contaminated wastewater from oil refining industry. The DACO experiments were carried out in a distillation batch reactor, using CuO/γ-Al₂O₃ as catalyst. The experimental temperature was kept at 100°C and H₂O₂ oxidant was supplied into the reactive system with 200 mL/L. The results demonstrated that more than 92.2% of chemical oxygen demand removal was obtained and the absorbance of the refinery wastewater after treatment was zero, indicating significant decolorization efficiency for the solution. The research of life and stability showed that the catalyst had a good stability. The present study indicates that this DACO approach may have a significant application potential for industrial wastewater treatment.

Key words | catalytic oxidation, combined process, distillation, wastewater treatment

INTRODUCTION

Wastewater from petroleum refinery has the characteristics of high concentration of aliphatic and aromatic petroleum hydrocarbons, which could lead to a serious discharge problem due to their poor biodegradability, high toxicity and ecological aspects (Diaz et al. 2007; John Kennedy et al. 2007). The traditional treatment of refinery wastewater is based on the physicochemical and mechanical methods and further biological treatment in the integrated activated sludge treatment unit (Haarstrick et al. 1996; Leiknes & Semmens 2000; Bahnemann et al. 2002; Chen et al. 2003; Saini & Nejati 2007). With respect to the fact that different concentrations of aliphatic and aromatic petroleum hydrocarbons are present in the wastewater, among which the aromatic fraction is not readily degraded by conventional treatments and is more toxic, there is still a need for advanced techniques to remove non-biodegradable, high concentration organic substances of petroleum refinery wastewater as much as possible.

Catalytic wet oxidation (CWO) is an attractive technique to degrade non-biodegradable organic substances in industrial wastewater (Lei et al. 1997). Typical conditions (e.g. temperature and pressure) for conventional CWO are varying from 180 to 315°C and 2 to 15 MPa, respectively. The chemical oxygen demand (COD) removal can be achieved to 75–90% (Zimmerann 1950). Under CWO conditions, insoluble organic substance can be converted to simpler soluble organic compounds which are in turn oxidized and eventually converted to carbon dioxide and water (Sahibzada et al. 1996). Although conventional CWO method has been widely used, there are several drawbacks in that it requires severe operation conditions, such as high temperature, high pressure, and noble metallic catalysts (Luck 1996, 1999), which mean higher energy consumption and expensive running costs. These disadvantages have restricted its widespread application in the developing countries or for small enterprises. It is of significance to innovate the technology combining with CWO, aiming at effective treatment of industrial wastewater under milder conditions.

Therefore, we researched a combined process – distillation-assisted catalytic oxidation (DACO) technology to treat petroleum refinery wastewater. The DACO process was a coupling technology of catalytic oxidation and distillation, which made use of the advantages of these units to effectively solve questions that a single operation could not...
overcome in wastewater treatment process, and to achieve the purpose of the comprehensive management. It is worth mentioning that the process was a new research in the treatment of petroleum refinery wastewater and it used inexpensive and recoverable catalysts.

EXPERIMENTAL

Materials and preparation of catalysts

Reagent grade chemicals were obtained from commercial sources and used without further purification. Distilled water was used to prepare aqueous solutions. The \( \gamma \)-Al\(_2\)O\(_3\) support was prepared with minor modifications to the literature method (Vaidya & Thakkar 2001; Junwei et al. 2002; Zhaorong et al. 2002). Supported catalysts of metal loading were prepared by impregnating \( \gamma \)-Al\(_2\)O\(_3\) with aqueous solutions of Cu (NO\(_3\))\(_2\)·6H\(_2\)O to form a thick paste. The samples were then dried for 12 h at 353 K, followed by calcinations in air at 623 K for 3 h. For simplicity, these catalysts would hereafter be denoted as CuO/\( \gamma \)-Al\(_2\)O\(_3\).

Petroleum refinery wastewater was collected from Yan’an Petroleum Chemical Company, China. The chemical characteristics of wastewater are shown in Table 1.

Experimental method

A distillation batch reactor (Tianjin University Beiyang Chemical Engineering Co., China) was adopted for the experimental apparatus. Petroleum refinery wastewater was charged into the inner reactor by water pump, H\(_2\)O\(_2\) and supported catalysts were added before reaction, thereafter the reaction pressure was adjusted. The liquid sample in the reactor was heated by electric jacket as a reboiler to the desired temperature. During the experiment, liquid samples of top-column were periodically withdrawn and analyzed to determine COD concentrations. At the end of each experiment, the residue of catalysts were filtered off and washed with distilled water, then dried for 12 h at 353 K to analyze the structure and mass. All the experiments were repeated to check reproducibility of results. The data reported in this work were the arithmetic average of the results derived from three repeated DACO experiments.

Analytic method

COD was measured by the National Standard Methods (China, 1982) and the COD values of the petroleum refinery wastewater samples were 5,000 mg/L. The temperature variations in the reactor during DACO were recorded with a sheltered type-K thermocouple probe, and the pressure variations were controlled by U-type differential pressure instrument. The structure of the catalyst was determined by 7,000 X-ray diffractometer using Japanese Shimaozzi Co. The UV-Vis spectra were analyzed by 2,550 UV-Vis spectrophotometer using Japanese Shimadzu Co.

RESULTS AND DISCUSSION

Effect of different experimental processes on COD

In order to investigate COD degradation efficiencies of different processes for petroleum refinery wastewater, the following three experiments were carried out under the conditions of (1) 100 °C, atmospheric pressure, distillation process, (2) 100 °C, atmospheric pressure, 30 g/L CuO/\( \gamma \)-Al\(_2\)O\(_3\), 200 mL/L H\(_2\)O\(_2\), CWO process, and (3) 100 °C, atmospheric pressure, 30 g/L CuO/\( \gamma \)-Al\(_2\)O\(_3\), 200 mL/L H\(_2\)O\(_2\), DACO process, respectively. Figure 1 shows the results of COD removal ratio under different processes. In process (1), only 15.6% of the COD removal rate was reached in 90 min; in process (2), there was 59.7% of the COD removal rate could be obtained in 90 min by CWO; in process (3), the COD concentration of petroleum wastewater decreased significantly, and the COD removal rate reached 57.5% within 45 min, and subsequently the removal of COD increased to 92.2% within 90 min.

It could be seen that DACO approach results in the enhancement of COD removal rate (process (3)) compared to process (1) and process (2). The process (1) was only physical distillation operation, which used the difference of components volatility to achieve separation process. The process (2) was conventional CWO approach, which

<table>
<thead>
<tr>
<th>Item</th>
<th>Oil (mg/L)</th>
<th>Volatile hydroxybenzene (mg/L)</th>
<th>COD (mg/L)</th>
<th>NH(_3)-N (mg/L)</th>
<th>S(^2) (mg/L)</th>
<th>CN (mg/L)</th>
<th>Suspension substance (mg/L)</th>
<th>PH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average value</td>
<td>92</td>
<td>135</td>
<td>5,000</td>
<td>215</td>
<td>45</td>
<td>2</td>
<td>220</td>
<td>8.2</td>
</tr>
</tbody>
</table>
used CuO/γ-Al2O3 as a catalyst that catalyzed H2O2 to reaction with contaminants. However, process (3) was DACO operation, which combined the technology of the catalytic oxidation (process (2)) operation and distillation operation (process (1)), and used the advantages of these units to effectively degrade COD of refinery wastewater. As a result, this coupling process solved questions that the single operation could not overcome, and to achieve the purpose of the comprehensive management.

It could be concluded from the above results, the DACO, due to the combined effect of catalytic oxidation reaction and distillation, accelerated the oxidation reaction speed of contaminants in a closed reaction system, and had a good applicability to treat refinery wastewater.

The decolorization of different processes

In order to investigate decolorization efficiencies of different processes for refinery wastewater, we analyzed the decolorization efficiencies of solution after different oxidative degradation processes. Figure 2 shows the results. By analyzing the Figure 2, the CuO/γ-Al2O3 had better decolorization effect for oxidative degradation of the refinery wastewater, and the coupling of catalyst (CuO/γ-Al2O3) and oxidant (H2O2) was optimal, the absorbance was almost zero. Therefore the DACO in the purification of refinery wastewater had better decolorization effect.

The structure analysis of catalyst samples

The XRD patterns of the material samples in fore-and-aft reaction are shown in Figure 3. Figure 3 indicated the presence of the crystal phase of γ-Al2O3 and CuO, respectively. The structure and character of catalysts had an important impact for the dispersion and the existence state of the active component (Tieman & Finalayson 1998; Teschner et al. 2001; Santos et al. 2005). From the XRD spectra of CuO/γ-Al2O3 catalyst, no peaks for any other phases or impurities were detected. It showed that CuO/γ-Al2O3 had excellent catalytic activity.
Comparing the catalyst structure after reaction (see Figure 3(a)) to before reaction (see Figure 3(b)), there was the dispersion peak in the scope of $2\theta = 40^\circ \sim 80^\circ$, there was no change of peak shape, and no appearance of characteristic peaks of unknown substance, but the intensity of characteristic peaks was weakened; meantime the width of characteristic peaks of the samples expanded: the half-width of peaks were 0.76$^\circ$ and 0.92$^\circ$ ($2\theta = 48.6^\circ$) in the process of fore-and-aft. This might be due to the grain size of catalyst becoming smaller and more dispersed after reaction. Therefore, the chemical structure of catalyst becoming reaction was identical to before reaction. This would validate that the CuO/γ-Al2O3 catalyst had a good life and stability.

Table 2 showed that, the activity of CuO/γ-Al2O3 catalyst has declined since using three times, but it still kept higher activity. After being used five times, the recovery was basically little changed. It was likely that the halfway operation resulted in loss of about 15% catalysts during the recovery. So, it indicated that the catalyst was relatively stable and could be continuously applied in the treatment of refinery wastewater.

The technologic condition of DACO experiments

The choice of CuO/γ-Al2O3 catalyst dosage

Although the CWO reaction was very successful in the treatment of wastewater, it must be operated under relatively severe conditions in order to achieve a high COD removal efficiency (Leiknes & Semmens 2000). Adding catalysts into CWO process was one of the most popular options to reduce the temperature and pressure (Luck 1996, 1999; Lei et al. 1997). A series of experiments was carried out to find the influence of CuO/γ-Al2O3 catalyst dosage. Results obtained from experiments with varying catalyst amount from 0 to 45 g/L were illustrated in Figure 4. There was obvious improvement in the COD removals when the CuO/γ-Al2O3 catalyst dose increased from 0 to 30 g/L. A possible explanation was that increased catalyst amount of the solution enhanced reaction probability between the active site of catalyst surface to contaminations, so that the degradation was accelerated. However, the rate of reaction was found in some cases to be falling slowly or becoming nearly independent of amount, as CuO/γ-Al2O3 catalyst amount exceeded 30 g/L. The results were in agreement with those reported in the literature (Mengyne et al. 1995; Rideh et al. 1997; Bickley et al. 2005) for different organic materials. Thus, the efficient use of power and the optimization of catalyst concentration are key factors in achieving a satisfactory design.

The choice of H2O2 oxidant dosage

Results obtained from experiments with varying oxidant amount from 0 to 300 mL/L were illustrated in Figure 5. From Figure 5, it can be easily concluded that there is an improvement of COD removal rate of petroleum wastewater with increase of H2O2 amount. H2O2 in liquid phase could also induce oxidative free radicals (such as OH) under high temperature and high pressure. The oxidative free radicals have strong capacity to oxidize organic substances even into the degree of mineralization. The heat energy could cause locally higher temperature in some micro-surfaces of the CuO/γ-Al2O3 particles than water bulk. So, increasing H2O2 amount benefited the oxidation reaction. When the amount of H2O2 was 0 mL/L, using distillation-oxidation process, the catalyst could be added separately to reduce the COD value of refinery wastewater. The COD removal rate under 200 mL/L was similar to that under 300 mL/L, might be because there was already sufficient oxidant in
the reaction system under 200 mL/L. At the same time, high amount of H₂O₂ (over 200 mL/L) could enhance the running risk and cost of the operation. Therefore, 200 mL/L of H₂O₂ amount was chosen as optimal parameter in the work.

The operating temperature

Reaction temperature was a vital factor in the catalytic oxidation process, the depth of the oxidation of wastewater depended primarily on the maximum temperature which the oxidation reaction could reach (Pintar & Levec 1992). The higher the temperature is, the more intense the molecule movement, and the greater the chemical reaction rate. At the same time, the temperature had a significant impact for mass transfer rate. However, high temperatures would lead to an increase in energy consumption, synchronously, the reactor capability of acid-resistant and compression resistance would increase. So, from economic view, the optimal temperature was 100 °C in atmospheric pressure boiling points of water.

The operating pressure

The enhancement of pressure would increase the driving force of oxidation, and accelerate the reaction rate (Sun et al. 2008). However, high pressure also would enhance the running risk and cost of the operation. So, from economic view, we choose the atmospheric pressure as optimal pressure. Under this condition, the COD removal rate could reach more than 92.2% by DACO.

The operating time

From the experiments above, it could be seen that the value of the COD removal rate within 120 min was equal to the value within 90 min appreciatively. It indicated that those processes completed within 90 min, and there were no enhancements of COD removal rate and would only increase energy consumption if we extend time.

CONCLUSIONS

DACO process was an effective process for the removal of non-biodegradable organic substances in refinery wastewater. The process was demonstrated to be a suitable treatment method for biodegradation because the COD removal rate of wastewater was significantly increased. The experimental results revealed that non-biodegradable organic substances removal is enhanced by catalytic oxidation reaction and distillation. This process can be operated under milder pressure and temperature. Therefore, it will reduce the operation risk resulting from high pressure and high temperature within conventional CWO.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support from Shanxi Natural Science Foundation of China (Project No. 09JK816, 09JS064).

REFERENCES


