

Advanced oxidation processes with coke plant wastewater treatment

A. Krzywicka and A. Kwarciak-Kozłowska

ABSTRACT

The aim of this study was to determine the most efficient method of coke wastewater treatment. This research examined two processes – advanced oxidation with Fenton and photo-Fenton reaction. It was observed that the use of ultraviolet radiation with Fenton process had a better result in removal of impurities.

Key words | advanced oxidation process, coke wastewater

A. Krzywicka (corresponding author)
A. Kwarciak-Kozłowska
Institute of Environmental Engineering,
Czestochowa University of Technology,
Brzeznicza 60a,
42-200 Czestochowa,
Poland
E-mail: aleksandra.krzyw@gmail.com

INTRODUCTION

The main source of coke plant wastewater is the coal coking process. Industrial wastewater contains a large amount of recalcitrant compounds which are generally phenol, ammonia, heterocyclic compounds and cyanide (Li *et al.* 2003; Mielczarek *et al.* 2011). These constituents could have a toxic effect on a variety of organisms (Sindera *et al.* 2011). Generally the effluent is discharged into a natural water receiver or municipal wastewater plant. For this reason, it is required to fulfil the industrial wastewater quality standards. Several methods have been examined to improve the wastewater quality. An activated sludge process is not effective in industrial wastewater treatment because of microorganism sensitivity to its compounds. Especially phenol can inhibit biological processes (Marañón *et al.* 2008). The advanced oxidation processes (AOPs) are an alternative to biological methods in terms of elimination of non-biodegradable pollutants (Chitra *et al.* 2011). The advanced methods include Fenton and photo-Fenton processes ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{ultraviolet}$ (UV), respectively). UV radiation with hydrogen peroxide or without it also are classified as AOPs (Hamad *et al.* 2005, Kwarciak-Kozłowska *et al.* 2011). The main goal of these processes is to generate highly reactive hydroxyl radicals ($\cdot\text{OH}$), which could oxidize most of the wastewater organic compounds. The biodegradability of the organic constituent is improved with the radical mechanism. In acidic conditions, which prevent $\text{Fe}(\text{OH})_3$ precipitation, reactive hydroxyl radicals are generated by catalytic degradation of hydrogen peroxide. It is very important to select the appropriate dose of catalyst (Fe^{2+}) and hydrogen peroxide, because the excess of hydrogen peroxide may react with $\cdot\text{OH}$ instead

of with pollutants. This chemical process is called the scavenging reaction (Schrank *et al.* 2005; Barbusiński 2009; Omar *et al.* 2010).

The coke wastewater used in this research was collected from a local coke industry. One of the pollutant indicators, chemical oxygen demand (COD), was at the level of $7,985 \text{ mgO}_2/\text{dm}^3$. The biological oxygen demand (BOD_5) was $10 \text{ mgO}_2/\text{dm}^3$. The wastewater was characterized with alkaline pH (8.83). Value of BOD_5/COD ratio was 0.0012, which indicated its extremely low biodegradability. Table 1 provides a summary of raw sewage indicator values.

METHODS

The first part of the research included determination of the most appropriate $\text{COD}/\text{H}_2\text{O}_2$ ratio. Based on the review of the literature and economical consideration it was decided that the $\text{COD}/\text{H}_2\text{O}_2$ weight ratio shall be 1/2. The main objective of this research was to determine which method is preferable for use in coke wastewater treatment. This aim was achieved by comparison of organic pollutants removal effectiveness.

Two advanced oxidation methods were used in this research. First, the classical Fenton process was examined. In this step of research four doses of reagents were tested. The $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio values ranged from 20:1 to 2.5:1. This process was carried out in several stages. The first stage consisted of acidification to pH of 3.0. Then was added $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in different amount followed by rapid mixing for 5 min. The third stage included the addition of

Table 1 | Characteristics of raw sewage from a coke plant

Pollution indicator	Value in raw wastewater	Permissible standards for natural receiver ^a
pH	8.33	6.5–9.0
COD, mgO ₂ /dm ³	7,985	250
TOC, mgC/dm ³	1,290	30
TN, mgN/dm ³	1,840	30
Ammonium nitrogen, mgNH ₄ ⁺ /dm ³	672	10

^aPolish Ministry of Environment (2009).

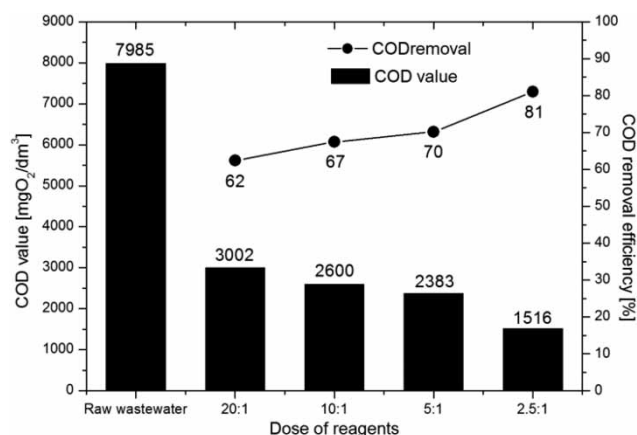
H₂O₂ and mixing at the same conditions. After 3 hours of slow mixing the wastewater sample was neutralized. The parameters were determined after 3 h of sedimentation.

The next process was photo-Fenton oxidation. In this process the same H₂O₂/Fe²⁺ ratios were examined. The research steps were similar to Fenton process. In the slow mixing phase the UV radiation's source was a UV lamp submerged in the reactor.

The chemical indicators were determined according to Polish Standards. COD, total organic carbon (TOC), total nitrogen (TN), and ammonia nitrogen were analysed both in raw and treated wastewater. The 10C Kiper TOC Analyzer PX120 was used to measure the TOC and TN amount. Ammonia nitrogen was determined with the distillation method. The COD was determined in accordance with the colorimetric method.

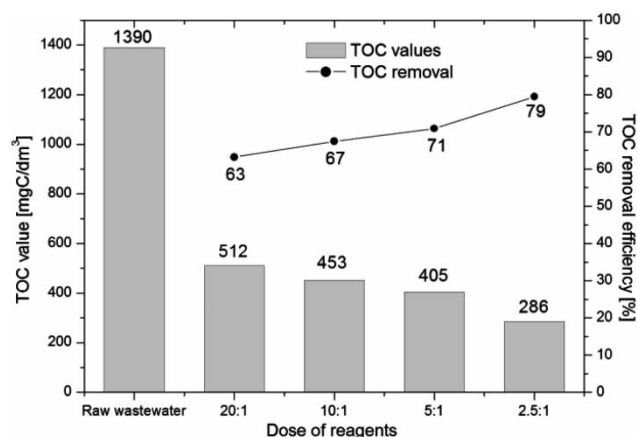
RESULTS AND DISCUSSION

The COD value in raw coke wastewater was 7,985 mgO₂/dm³. It was found that decreasing H₂O₂/Fe²⁺ ratio resulted in decreasing the COD value. The best result was obtained at 2.5:1 (H₂O₂/Fe²⁺) dose of reagents. Under these conditions the COD value was at the level of 1,516 mgO₂/dm³ (81% COD removal efficiency). Further reducing the weight ratio of iron to hydrogen peroxide resulted in increasing amounts of catalyst (iron sulfate), which causes the formation of a larger amount of iron hydroxide sludge. The eight-fold lower catalyst dose (20:1 H₂O₂/Fe²⁺) resulted in 19% lower COD removal efficiency. The COD amounted to 3,002 mgO₂/dm³. Generally it was observed that reduction of catalyst with the constant amount of H₂O₂ contributed to an increase in COD removal level. These results are shown in Figure 1.

**Figure 1** | COD value and removal efficiencies in coke wastewater treated in Fenton process.

The same relationship was observed with TOC level. In raw wastewater the TOC value was 1,390 mgC/dm³. Increasing the dose of FeSO₄·7H₂O in the reaction tank resulted in increasing of organic carbon removal efficiency. The most appropriate dose of reagents was 2.5:1 H₂O₂/Fe²⁺. At the higher dose of catalyst (6.4 g Fe²⁺/dm³) the TOC removal rate was 79% and it was the highest removal efficiency. Under these conditions the TOC value was 286 mgC/dm³ and was 4.5-fold lower than in raw wastewater (1,390 mgC/dm³). The lowest removal rate at the level of 63% (512 mgC/dm³) was observed after application of 20:1 H₂O₂/Fe²⁺ reagents dose. Inorganic carbon was only 139 mgC/dm³ in raw wastewater and was removed by almost 100% (99% at 2.5:1 H₂O₂/Fe²⁺). The TOC value and reduction amount are shown in Figure 2.

The AOP did not eliminate the ammonium and TN. In raw wastewater these indicators were at the level of

**Figure 2** | TOC value and removal efficiencies in coke wastewater treated by Fenton process.

672 mgN-NH₄⁺/dm³ and 1,849 mgN/dm³, respectively. The TN removal did not achieve 20% for all doses and was 14.4% on average. The higher ammonium nitrogen removal rate was 19% (10:1 H₂O₂/Fe²⁺).

Wastewater coke treatment with Fenton process resulted in sludge production. Increasing the rate of Fe²⁺ in the reagent tank resulted in increased precipitation of its chemical sludge. After application of the most appropriate dose of reagents (2.5:1 H₂O₂/Fe²⁺), the sludge volume amounted to 50% by volume of wastewater and its dry weight was 20.35 g/dm³.

The second part of the research included Fenton reaction with UV radiation. The results obtained at this stage of research was different from the previous reaction. Increasing the Fe²⁺ dose in the reaction mixture reduced the elimination of impurities referred to as TOC and COD. Wastewater treated with the photo-Fenton process resulted in on average 70 and 80% removal of COD and TOC, respectively. It was found that the most suitable dose of reagent was 20:1 H₂O₂/Fe²⁺. At this dose of reagents COD and TOC values were 1,879 mgO₂/dm³ and 221 mgC/dm³, respectively. It indicated that COD removal efficiency reached the level of 76%, and TOC was eliminated by 84%. The TOC and COD reduction are shown in Figures 3 and 4, respectively.

The photo-Fenton reaction did not eliminate nitrogen from the coke wastewater. TN including ammonium nitrogen were removed by an amount below 15%. The higher TN and ammonium nitrogen removal efficiency (14 and 11%) was achieved at 2.5:1 H₂O₂/Fe²⁺.

At optimal reagent dose (20:1 H₂O₂/Fe²⁺) sludge production was 140 cm³/dm³ and its dry weight was 20.09 g/dm³. Wastewater treatment with higher dose of reagents resulted

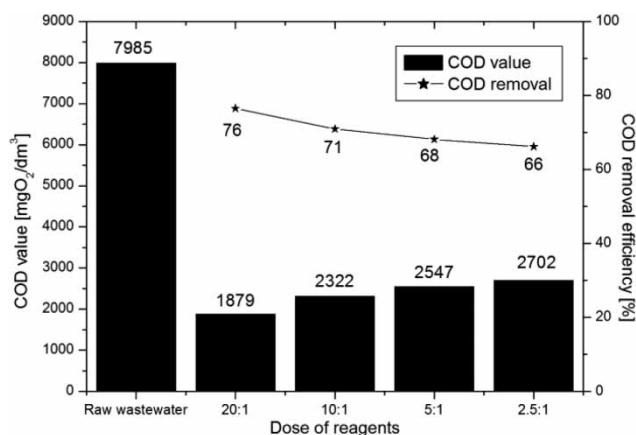


Figure 3 | COD values and removal efficiencies in photo-Fenton treated wastewater.

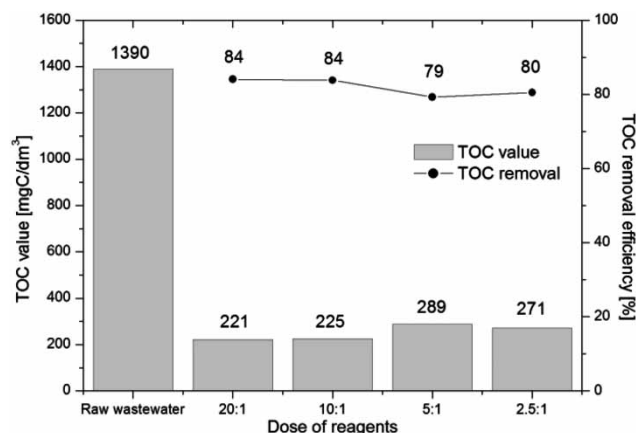


Figure 4 | TOC values and removal efficiencies in photo-Fenton treated wastewater.

in significant increase in sludge production (820 cm³/dm³ after 3 hours of sedimentation for 2.5:1 H₂O₂/Fe²⁺).

COMPARISON OF FENTON AND PHOTO-FENTON PROCESSES IN TERMS OF IMPURITIES REMOVAL

The use of the best dose of reagents in Fenton process – 2.5:1 H₂O₂/Fe²⁺ – resulted in 14% higher COD removal efficiency in comparison to the same dose in photo-Fenton process. At this dose of reagents the COD value was 1,516 mgO₂/dm³ for Fenton process and 2,702 mgO₂/dm³ for Fenton process with UV radiation. On the other hand, the best ratio of H₂O₂ and Fe²⁺ was 20:1 for photo-Fenton process. Under these conditions, the sludge production was the lowest (140 cm³/dm³) in comparison with the optimal dose of reagents in Fenton process. The COD value reached the level of 1,879 mgO₂/dm³ and was greater by 364 mgO₂/dm³ than the best Fenton process result (1,516 mgO₂/dm³). Removal efficiency of COD after photo-Fenton process was lower by 4.6% in comparison to Fenton process at optimal reagent dose.

Generally photo-Fenton reaction at every dose of reagents resulted in higher TOC elimination. Application of the photo-Fenton process with 20:1 reagent ratio led to preferable TOC reduction in treated wastewater. The TOC value reached the level of 221 mgC/dm³ and removal efficiency was 84%, while using the optimal ratio in Fenton process (2.5:1) this indicator was 286 mgC/dm³ and removal efficiency reached the level of 79%.

Results have shown that the higher the dose of ferrous sulphate added, the greater the amount of sludge produced. It was also found that the photo-Fenton process results in lower sludge production. At 20:1 H₂O₂/Fe²⁺ in

photo-Fenton process the volume of sludge was 3.6-fold lower than at the best dose (2.5:1) of reagents in classical Fenton process. This sludge should be properly managed. Iron hydroxide sludge can be dewatered, dried, baked and dissolved in sulfuric acid to regenerate the catalysis according to the method proposed by Cao *et al.* (2009).

CONCLUSIONS

Coke plant wastewater contains a great amount of low biodegradable pollutant. AOPs like classical Fenton reaction or Fenton-UV process have contributed to reduction of impurities. The first stage of research has shown that application of the higher dose (2.5:1) of catalyst (Fe^{2+}) in relation to the source of reactive radicals (H_2O_2) resulted in the higher removal of pollutants. Although the Fenton process gave better results in COD value reduction, the problem was with high sludge production. Research indicates that the more efficient method for coke plant wastewater treatment was the photo-Fenton process. At the optimal reagent ratio – 20:1 $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ – the ferrous sulphate addition was minimized, which resulted in slight production of sludge. TOC and COD removal efficiencies were 76 and 84%, respectively; however, the permissible standards were exceeded. It indicates that these AOPs should be modified or supported with other methods. Fenton and photo-Fenton processes may be considered as pre-treatment processes of biological treatment.

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