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COKE PLANT WASTEWATER TREATMENT BY FENTON REAGENT

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OCZYSZCZANIE ŚCIEKÓW KOKSOWNICZYCH Z WYKORZYSTANIEM ODCZYNNIKA FENTONA

Rzeczywiste ścieki koksownicze były efektywnie oczyszczane z wykorzystaniem odczynnika Fentona. Najkorzystniejsza dawka H_2O_2 i stosunek Fe^{2+}/H_2O_2 wynosiły odpowiednio 5 g/dm³ i 0,2 przy pH 3,5. Najszybsze obniżenie wartości ChZT oraz stężenia fenoli, cyjanków i rodanków uzyskiwano w ciągu pierwszych 20 minut reakcji Fentona. Jednak w celu uzyskania obniżenia toksyczności ścieków do niskiego poziomu (na bazie testu z bakteriami bioluminescencyjnymi *Vibrio fischeri NRRL B-11177*), konieczne było wydłużenie czasu reakcji do 2 godzin. Szybsze zmiany wartości ChZT oraz stężenia fenoli, cyjanków i rodanków w porównaniu ze zmianami toksyczności można tłumaczyć istotnym wpływem na poziom toksyczności pośrednich produktów rozkładu zanieczyszczeń powstających podczas reakcji Fentona. Badania wykazały, że zastosowanie odczynnika Fentona może być brane pod uwagę jako odpowiedni sposób podczyszczania ścieków koksowniczych. W celu minimalizacji kosztów i maksymalizacji efektywności procesu, dalsza optymalizacja sposobu oczyszczania powinna brać pod uwagę zastosowanie kombinowanych procesów chemiczno-biologicznego utleniania.

Summary

The real coke wastewater was effectively treated using Fenton reagent. The most advantageous dose of H_2O_2 and Fe^{2+}/H_2O_2 ratio were 5 g/dm³ and 0.2, respectively at pH 3.5. The fastest reduction of COD, phenol, cyanides and thiocyanates was received within the first 20 minutes of Fenton reaction. Nevertheless, in order to achieve the reduction of wastewater toxicity to low toxic level (test using bioluminescent bacteria *Vibrio fischeri NRRL B-11177*); it was necessary to increase the reaction time to 2 hours. More rapid changes of COD, phenol, cyanides and thiocyanates than in the case of changes in toxicity level, may indicate that toxicity is significantly influenced by intermediates that are formed during Fenton reaction. It was concluded that the Fenton oxidation can be considered as a suitable option for the effective pretreatment of coke plant wastewater. However, in order to minimize costs and maximize treatment efficiency, further optimization of treatment system would take into consideration use of combined chemical and biological oxidation process.

INTRODUCTION

In coke plant, the coal is converted to coke, which is suitable for metallurgical industries. The effluents from coke plant are of three basic types [7]:

- water used for quenching the coke discharged from the retorts or ovens,
- waste formed during cooling and washing the gas,
- waste formed during the purification of by-products.

These effluents are highly polluted and extremely difficult to treat because of large quantities of toxic compounds and coal-derived liquors. Coke plant wastewater contains large amount of suspended solids, high COD, BOD, and high concentrations of phenols, ammonia and other toxic substances (e.g. polynuclear aromatic hydrocarbons – PAHs, thiocyanates, cyanides and naphthalene) [7, 13].

The processes for treatment of coke plant effluent occur in various combinations in different systems, but in most cases wastewater treatment system consists of physico-chemical and biological processes. Conventional activated sludge system for coke plant wastewater treatment is not efficient in reducing COD to meet the discharge standard because of the presence of refractory organics. Nitrification is also difficult to proceed in the aeration tank of a conventional system because many typical compounds in coke plant wastewater are inhibitory to nitrobacter at certain concentrations [24]. As it is known, in a combination of chemical and biological degradation systems, chemical pretreatment usually enhances the biological process [22]. Therefore, it is crucial that simple and effective methods of chemical treatment of coke plant wastewater are researched as they will facilitate and improve the efficiency of their further biological treatment.

The Fenton reagent (H_2O_2/Fe^{2+}) has been found to be effective in degradation of various industrial wastewater components [2, 6, 8, 10, 11, 14, 16]. Therefore, the Fenton reagent has been applied to treat a variety of wastes such as those associated with the textile and chemical industry. This method offers a cost-effective source of hydroxyl radicals, using easy-to-handle reagents [15]. This paper presents the results of laboratory experiments that were carried out on coke plant wastewater to pretreatment them effectively by Fenton reagent.

MATERIALS AND METHODS

Coke Wastewater: The wastewater was collected from coke plant in southern Poland. It was characterized by a light brown color and medium clarity. Characteristics of wastewater used in this study are presented in Table 1.

Table 1. Characteristics of the coke plant wastewater used in this study

Parameters	unit	value
COD	mg O_2/dm^3	3334 – 4332
Phenol	mg/dm^3	216 – 228
Cyanides	mg/dm^3	442
Thiocyanates	mg/dm^3	1115
pH	–	8.9 – 9.0
Toxicity to *Vibrio fischeri*	%	100

Experimental procedure: The following parameters of Fenton reagent were examined and optimized: H_2O_2 concentration, Fe^{2+}/H_2O_2 ratio, pH and time. The procedure was as follows: coke wastewater was put into reactors of 2 dm^3 volume, and then acidified with H_2SO_4 to the selected value, as a Fenton reagent is effective in acidic pH range. After that, various doses of 30% H_2O_2 and solid $FeSO_4 \cdot 7H_2O$ were added with continuous magnetical stirring. After appropriate time the wastewater was neutralized with 5% solution of NaOH up to about pH 8.5.

Analytical methods: COD and other main pollutants (phenol, cyanides and thiocyanates) in coke wastewater were determined in accordance with Polish Standard [18–21], while pH was measured by pH-meter (pH-196, Poland). Toxicity was measured at optimal parameters of Fenton reagent, using a bioluminescent bacteria *Vibrio fischeri NRRL B-11177* (ToxAlert®10 instrument – Merck) as toxicity indicators. COD and toxicity tests were made after total removal of residual H_2O_2, using Na_2SO_3, as even a very low concentration of hydrogen peroxide resulted in inhibition of vital activity of bacteria *Vibrio Fischeri*. The residual H_2O_2 also increased the COD value since it acts as a reductant, especially in the chromate-based analysis of COD [1].

Concentration of residual H_2O_2 was analyzed by iodometric method. The initial light brown color of raw wastewater was not an obstacle in determination of H_2O_2 because, after Fenton reaction, the wastewater was discoloring.

RESULTS AND DISCUSSION

Effect of H_2O_2 dosage

The effect of the H_2O_2 dosage (from 1 to 10 g/dm^3) on COD and phenol removal efficiency is shown in Figures 1 and 2, respectively. The COD values and phenol concentrations were analyzed after 60 and 120 minutes of the Fenton oxidation. Both the COD and phenol removal efficiency were enhanced with increasing the dosage of hydrogen peroxide.

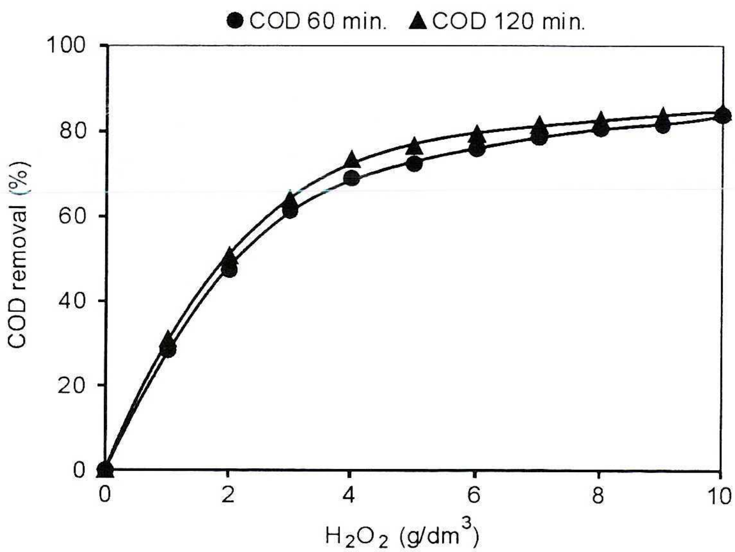

Fig. 1. Effect of the H_2O_2 dosage on the COD removal efficiency

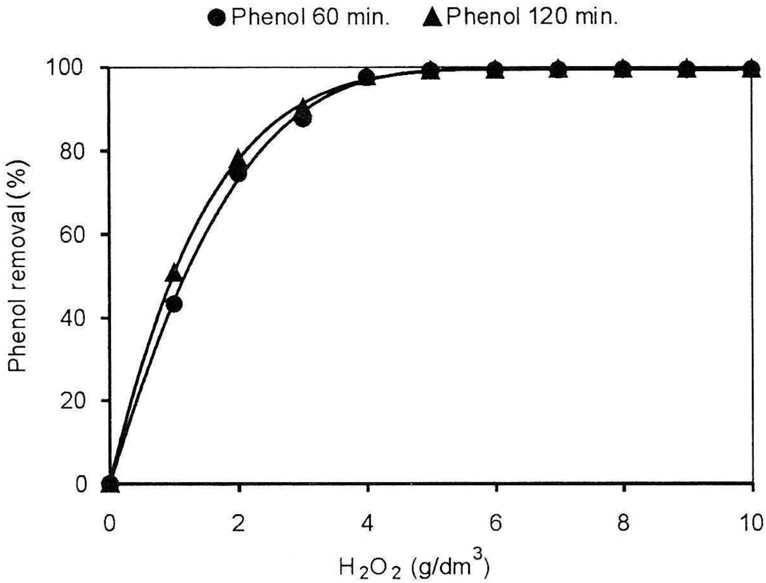

Fig. 2. Effect of the H_2O_2 dosage on the phenol removal efficiency

As the dosage of H_2O_2 increased from 1 to 5 g/dm^3 COD removal reached 72.5% (1176 mg/dm^3) and 76.6% (1000 mg/dm^3) after 60 and 120 minutes, respectively. When increasing the H_2O_2 dosage from 5 to 10 g/dm^3, COD removal efficiency increased to 83.8% (692 mg/dm^3) and 84.6% (656 mg/dm^3) after 60 and 120 minutes, respectively.

At the same time, the best results of phenol removal efficiency reached 99.2% (1.9 mg/dm^3) and 99.3% (1.8 mg/dm^3) at H_2O_2 dosages in the range of 1 to 5 g/dm^3 after 60 and 120 minutes, respectively. However, when the dosage of H_2O_2 exceeded 5 g/dm^3, only slight increase in phenol removal efficiency up to 99.4% (after 60 minutes) and 99.6% (after 120 minutes) was observed. As it has been observed, prolongation of reaction time from 60 to 120 minutes did not have a significant influence on the improvement of treatment effects. Therefore, further experiments concerning the optimization of pH and ferrous sulfate dosage were continued at H_2O_2 dose of 5 g/dm^3 and reaction time of 60 minutes.

Effect of $FeSO_4$ dosage

Further experiments concern the effect of Fe^{2+}/H_2O_2 ratio on COD removal and phenol degradation. Figure 3 presents the COD and phenol removal efficiency at different Fe^{2+}/H_2O_2 ratios using constant H_2O_2 concentration of 5 g/dm^3. These results show that at Fe^{2+}/H_2O_2 ratio in the range of 0.1–0.2 (2.49–4.98 g $FeSO_4$/dm^3), both COD and phenol removal efficiency significantly increases with an increase in Fe^{2+}/H_2O_2 ratio. The best results of COD and phenol removal (75.8% and 99.1% respectively) were achieved at Fe^{2+}/H_2O_2 ratio of 0.2. However, above Fe^{2+}/H_2O_2 ratio of 0.2, a slight decrease in COD and phenol removal was observed. This inhibitory effect at the higher Fe^{2+}/H_2O_2 ratio could be explained by an observation that excessive ferrous ions are the dominant hydroxyl radical's scavenger in the Fenton reaction [3, 23]. Further experiments concerning the optimization of pH were continued at Fe^{2+}/H_2O_2 ratio of 0.2.

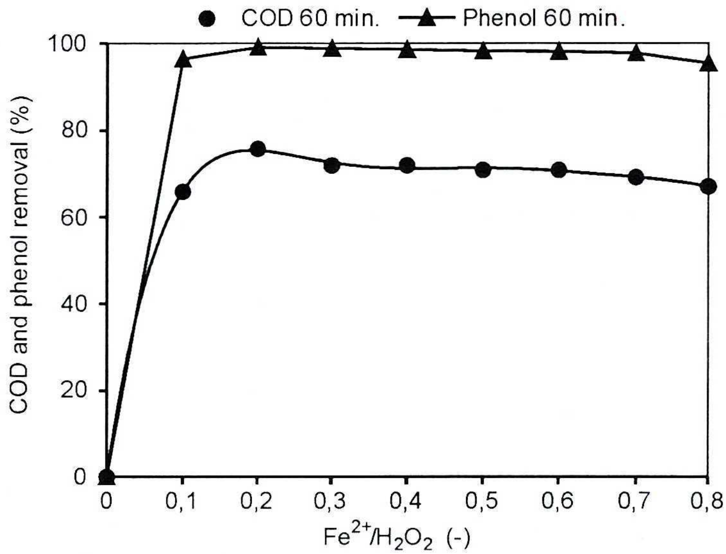

Fig. 3. Effect of the Fe^{2+}/H_2O_2 ratios on the COD and phenol removal efficiency

Effect of pH

As previous papers had reported, the pH in the range of 2.5–4.0 is highly important for effective Fenton oxidation [9, 12, 17]. In order to estimate the pH effect on COD and phenol removal, the experiments were conducted at pH values varying between 1 and 6. As presented in Figure 4, the best results of COD removal efficiency were achieved in the pH range 3–4 (74.3%). However, if the pH value dropped to the pH range 1–2, a substantial decrease in efficiency of COD removal was observed. These phenomena could be explained by the high excess of hydrogen ions, behaving as an OH · radical scavenger [3, 23].

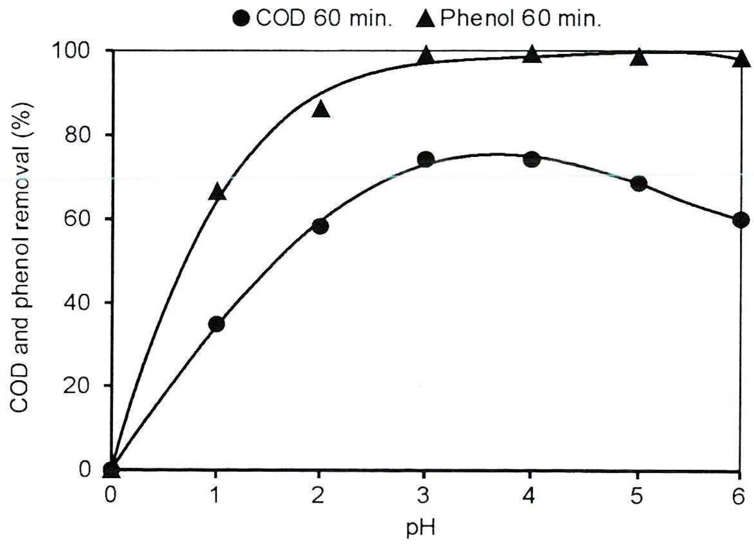

Fig. 4. Effect of the pH reaction on the COD and phenol removal efficiency

As the pH changed from 4 to 6 (Fig. 4), distinct decrease in COD removal efficiency was also achieved. A diminishing efficiency of Fenton oxidation at pH 5 and 6 was in accordance with other report, that near and above pH 4, the rapid hydrogen peroxide decomposition (probably on the surface of the ferric hydroxide floc), would not produce appreciable amounts of available hydroxyl radicals in the solution [5]. The COD removal efficiency was rapidly decreased not only by decomposition of hydrogen peroxide, but also by deactivation of a ferrous catalyst with the formation of ferric hydroxo complexes [4].

Figure 4 also shows the effect of the pH on the phenol removal efficiency in the Fenton oxidation. The best results of phenol removal efficiency (99.6–99.7%) were achieved in the pH range 3–5. Just like in the case of COD removal, if the pH value dropped to the pH range 1–2, the phenol removal efficiency was rapidly decreased to 86.3% at pH 2.0 and to 66.7% at pH 1.0. On the contrary, in a pH reaction higher than 5, the phenol removal efficiency was slightly decreased from 99.6% to 98.5%.

Effect of reaction time

In the second part of investigations, coke plant wastewater was treated at optimum parameters of the Fenton reaction obtained in the first part of experiments. Figure 5 shows the changes of COD, phenol, cyanides and thiocyanates during 2 hours of the Fenton oxidation. The analysis of time characteristics clearly showed that in all cases the fastest reduction of pollutants was received within the first 20 minutes of reaction time. After this time, COD and thiocyanates concentrations were slowly diminished to 882 mg O_2/dm^3 and 371 mg/dm^3 respectively within up to 120 minutes' and no substantial changes of phenol and cyanides were observed. The lowest values of phenol (0.5 mg/dm^3) and cyanides (2.6 mg/dm^3) were observed after reaction time of 2 hours, but for example, after 60 minutes these values were only a little greater (0.86 and 3.5 mg/dm^3 respectively).

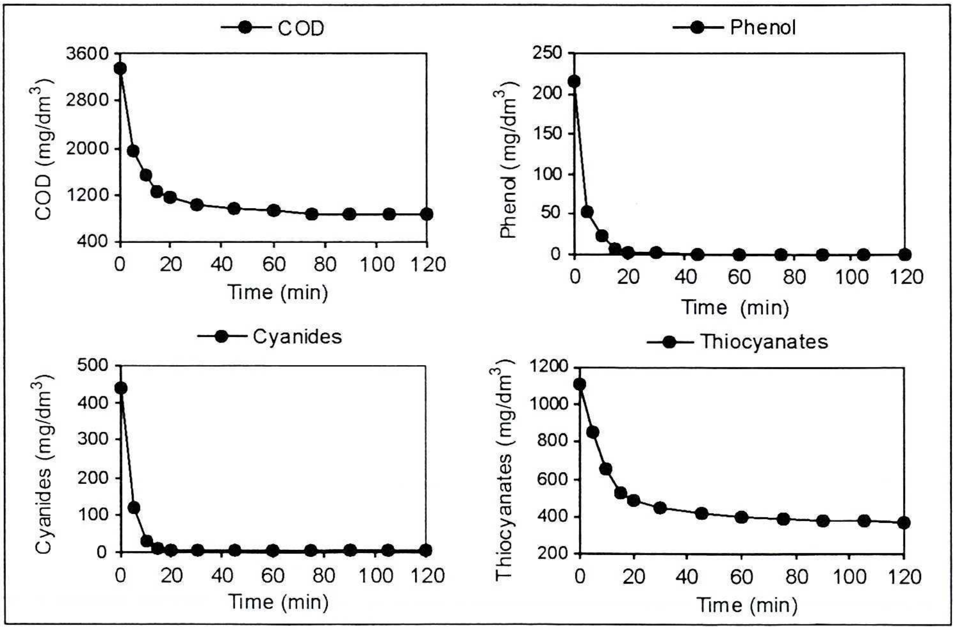

Fig. 5. Changes of the COD, phenol, cyanides and thiocyanates concentration in the effluent during 2 hours of the Fenton oxidation

Toxicity of wastewater

Toxicity of raw wastewater was very high and inhibited vital activity of bioluminescent bacteria *Vibrio fischeri* in 100%. After 15 minutes of the Fenton reaction time, a decrease in toxicity from 100% to 76% was observed. Prolongation of reaction time caused further distinct toxicity reduction to 48%, 31% and 24% after 0.5, 1 and 2 hours respectively. Two hours' reaction time was sufficient to achieve reduction in toxicity to low toxic level. The wastewater that causes inhibition of vital functions of bacteria *Vibrio fischeri* below 20% is considered as non-toxic when ToxAlert® 10 system is used.

The decrease of toxicity was not proportional to the drop of COD value and concentration of other main pollutants. More rapid COD, phenol, cyanides and thiocyanates changes than it was in case of changes in toxicity level, may indicate that toxicity is significantly influenced by intermediates which are formed during Fenton reaction. It can be assumed, that during Fenton reaction easily degradable substrates undergo oxidation at the beginning and then, more resistant compounds are oxidized. The latter substances most probably cause a slower rate of reduction of toxicity in the investigated wastewater.

CONCLUSION

On the basis of the above results it can be stated that the Fenton oxidation can be considered as a suitable option for the pretreatment of coke plant wastewater. Relatively significant effects of the COD and other main pollutants (as phenol, cyanides and thiocyanates) removal can be achieved in a short time. It may be therefore assumed that further biological oxidation will bring about significant effects, which will allow to safely discharge this wastewater to surface water bodies.

In the presented experiments, the decrease of toxicity was not proportional to the drop of COD and other analyzed parameters, but prolongation of reaction time caused distinct toxicity reduction to low toxic level. Moreover, as it is known, in a combination of chemical and biological degradation systems, chemical pretreatment usually enhances the biological process. Therefore it is very important that optimal parameters of using the Fenton reagent be chosen in order to enable effective functioning of combined treatment system.

Acknowledgements

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