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Study of gamma irradiation-induced effects on organic pollutants and suspended solids in coking wastewater

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ABSTRACT

To investigate the effects of gamma irradiation on coking wastewater treatment, a preliminary study using different doses of gamma radiation (1, 3, 5 and 7 kGy) on coking wastewater samples was carried out. The pH parameter, chemical oxygen demand (COD), total suspended solids (TSS) and total organic carbon (TOC) of the coking wastewater samples were determined before and after irradiation. Results showed that gamma irradiation was effective for removing organic contaminants and suspended solids particles. The values of COD, TSS, TOC and pH decreased with the increasing of absorbed doses, after gamma irradiation. The removal rate of TSS and TOC is 81.43 and 95.22% at the absorbed doses of 7 kGy, respectively. It indicates that gamma irradiation offers an alternative method for coking wastewater treatment that may have extra benefit of improving the water quality.

Keywords: Gamma irradiation; Coking wastewater; Chemical oxygen demand (COD); Total organic carbon (TOC); Total suspended solids (TSS)

1. Introduction

With the rapid development of coke industry, a large amount of coking wastewater was discharged into the environment annually. Coking wastewater is a kind of toxic and refractory industrial wastewater which is difficult to treat due to its complex composition. The coking wastewater usually contains high contents of various pollutants, both inorganic and organic. The inorganic pollutants are mainly large amounts of ammonium salt, cyanide, sulfide, etc. Organic pollutants include phenolic compounds, poly cyclic aromatic hydrocarbons and heterocyclic compounds of nitrogen, sulfur, and oxygen in organic compounds. Most of these pollutants are toxic, refractory, mutagenic, and carcinogenic [1,2]. Considering the large volume of coking wastewater, their discharge to environment can pose a potential threat to humans or ecosystem.

Conventional treatment of coking wastewater includes solvent extraction of phenolic compounds, steam stripping of ammonia, and biological treatment (mostly activated sludge process) [3–5]. However, such treatment processes cannot remove the refractory and toxic organic matter in coking wastewater effectively [5]. Meanwhile, these processes are accompanied with high cost of sludge treatment, disposal, activated carbon regeneration, as well as secondary pollution

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[1,6]. Although some new biological reactors and processes have been developed, and have improved the removal efficiency of organic matter and color [1,3–10], they still fail to meet current effluent discharge standards [10]. Therefore, new approaches should be taken to overcome this situation.

A number of investigations have reported that application of ionizing radiation with gamma rays to treat wastewater has its special properties and advantages. It is a simple and efficient technique that can remove a wide variety of organic contaminants and disinfect harmful microorganisms [11–19]. A few studies have successfully applied this technique in water and wastewater treatment to reduce color [15], chemical oxygen demand (COD) [11,15,17,20], and total organic carbon (TOC) of wastewater [15,18,21,22]. However, research on coking wastewater treatment using this technique has not been well explored.

The objective of this study is to investigate the effects of gamma radiation on coking wastewater with different absorbed doses by determining the changes of pH, COD, total suspended solids (TSS), and TOC content in the coking wastewater samples before and after radiation. The results of this study can provide useful information for evaluating the efficiency of gamma radiation-induced effect on coking wastewater and provide a theoretical basis for coking wastewater treatment with gamma radiation.

2. Materials and methods

2.1. Materials

The coking wastewater used in this work was sampled from Hengda Coal Gasification Company in Taigu.

2.2. Irradiation treatment procedure

Irradiation was conducted at room temperature (around 20°C) by a ^{60}Co source located at Shanxi Agricultural University. The radioactivity of the source was about 3×10^4 C_i, samples were irradiated with γ-rays at the dose rate of 2 Gy/min. The absorbed doses were 1, 3, 5, and 7 kGy. Each effluent sample of 500 ml was placed in the radiation field at a specific distance from the source to achieve the desired series of absorbed doses. Absorbed doses were determined by a silver dichromate dosimeter [19,22].

2.3. Analysis methods

The COD determination in coking wastewater was done using analysis with the potassium dichromate method (GB/T 11914-1989). TSS was determined by the weight method (GB 11901-1989). TOC was determined according to the combustion oxidation nondispersive infrared absorption method (GB 13193-1991). pH was determined by the glass electrode method (GB 6920-1986). All methods mentioned above were carried out according to the state standard of the People's Republic of China. Results are shown as the average of three replicates.

3. Results and discussion

3.1. Effect of gamma radiation on COD in coking wastewater

The oxidation effect of irradiation on organic pollutants in coking wastewater was expressed by determining the COD values. The COD values of the coking wastewater before and after irradiation were measured, and the relationship of the COD values and absorbed dose is shown in Fig. 1. It appears that COD values decrease at 3 kGy and increase again at higher doses. The results showed that 37.63% of COD was removed at the dose of 3 kGy, indicating higher treatment efficiency of organic pollutants in coking wastewater reached at this absorbed dose. Similar results have been reported and the decrease of COD values could be explained by the important oxidation and a partial destruction of complex or toxic organics in the wastewater [23,24].

It could also be found from Fig. 1 that though the COD values were gradually increased at the dose of 5 and 7 kGy, the COD values were inferior to that of the non-irradiated sample in all cases. The COD value increase at 5 and 7 kGy could be explained by the degradation of molecules induced by radiation, and the increasing of low-molecular weight substrates can facilitate the absorption of organic pollutants [15]. It has been reported that the quantity of pollutants

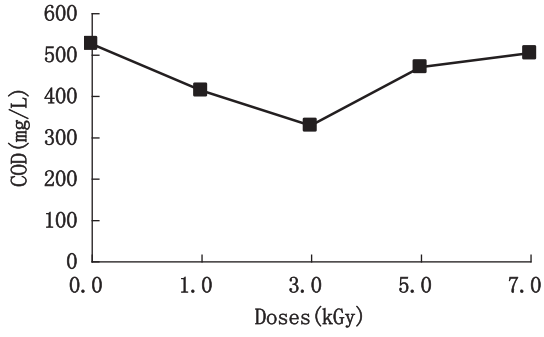

Fig. 1. Effect of gamma irradiation on the content of COD in coking wastewater effluents.

integrated or adsorbed to the particulate matter were non-negligible. In some cases, this is a major contribution to the coking wastewater COD [15]. Further studies should be performed to better understand the increase mechanism of COD at 3–7 kGy.

3.2. Effect of gamma radiation on TSS in coking wastewater

The gamma radiation induced the degradation of TSS of coking wastewater as shown in Fig. 2. Compared with control, the TSS concentrations of all irradiated samples at different doses had decreased significantly. At the absorbed dose of 1.0 kGy, the TSS value decreased from 120.6 to 108.0 mg/L and it continued to reduce with the increasing of absorbed doses. Compared with non-irradiated coking wastewater sample, the TSS value of coking wastewater by irradiation decreased about 10.45, 21.97, 51.74, and 81.43% at 1, 3, 5, and 7 kGy, respectively. Therefore, the reduction of TSS could be attributed to the gamma irradiation-induced effect (higher absorbed dose result in lower TSS value). The results indicated that TSS can be effectively decomposed at higher absorbed dose, which was similar to the results obtained by other authors [15].

3.3. Effect of gamma radiation on TOC in coking wastewater

The effect of gamma rays on the decomposition of organic pollutants in the coking wastewater was usually characterized by the reduction of TOC [18]. The changes in TOC values of coking wastewater before and after gamma radiation are exhibited in Fig. 3. It shows that the TOC value decreased with the increasing dose of gamma radiation from 1 to 7 kGy. Compared with the non-irradiated sample, the TOC value decreased from 420.3 to 208.7 mg/L, 106.1, 65.8, and 20.1 mg/L at the absorbed dose of 1, 3, 5, and 7 kGy, respectively, and the reduction rate was 50.34, 74.76, 84.34, and 95.22%, respectively. The results indicated that TOC in coking wastewater can be easily decomposed by using gamma radiation, which was in agreement with the conclusion obtained in other reports [15,18,21,22]. The efficient removal of TOC in coking wastewater during gamma radiation may suggest that gamma radiation leads to mineralization of organic matters.

The powerful oxidizing species of hydroxyl radical (·OH) could be produced by the interaction between gamma radiation and wastewater [15,21]. The aromatic rings of the coking wastewater would be attacked by the hydroxyl radical, and lead to decomposition of the ring structure, to transform into open chain alcohols, carboxylic acids, etc. The opened rings undergo further oxidation processes, and the final degradation products will be NH_4^+, NO_3^-, and NO_2^- [21], which result in the increasing of COD value.

3.4. Effect of gamma radiation on pH in coking wastewater

In general, coking wastewater contains ammonia, mixed ammonium salts, and nitrogen-containing heterocyclic compounds. High concentration of NH_3-N and mixed ammonium salts are among the main characteristics of coking wastewater, which result in the initial pH value of 9.73 [5,25].

Fig. 4 presents the changes in pH values in coking wastewater during gamma irradiation. It is obvious that the pH values of coking wastewater gradually decreased significantly with the increasing of absorbed

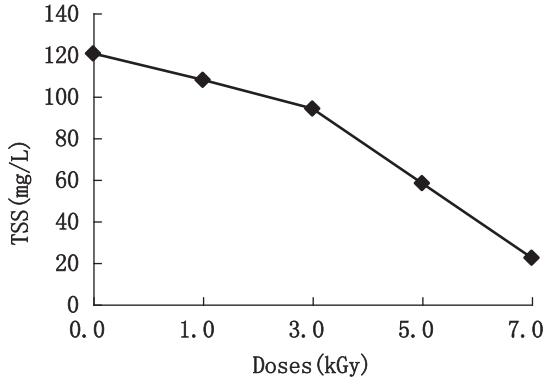

Fig. 2. Effect of gamma irradiation on the content of TSS in coking wastewater effluents.

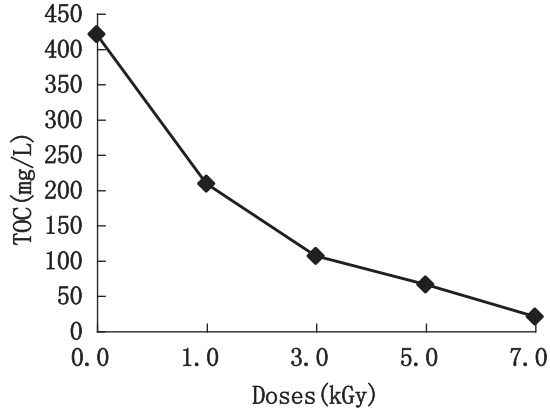

Fig. 3. Effect of gamma irradiation on the content of TOC in coking wastewater effluents.

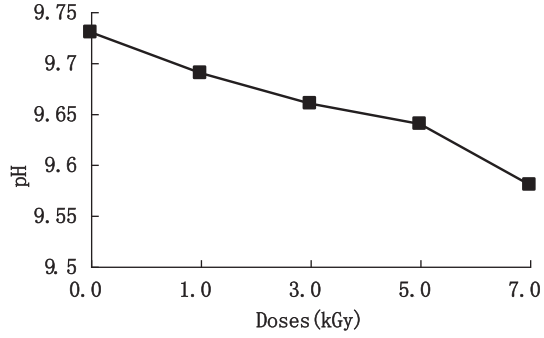

Fig. 4. Effect of gamma irradiation on pH value in coking wastewater effluents.

doses when compared with that of non-irradiated sample. With the increasing of absorbed doses, the reducing effect of using gamma radiation on pH in wastewater solutions has been already reported [11,17,19,22]. The rate of lowering of the pH is increasing with increasing absorbed doses in coking wastewater, compared to that of the control sample without gamma irradiation; the pH decreased from 9.73 to 9.69, 9.66, 9.64, and 9.58 at the absorbed doses of 1.0, 3.0, 5.0, and 7.0 kGy, respectively. The decrease of pH values most possibly may be attributed to the resulting formation of organic acids and carboxylic acids from the rupture of the organic compounds (such as phenol, benzene, toluene, etc.) that are transformed into smaller organics molecules during solution radiolysis [11,22].

4. Conclusions

The preliminary results of this study indicated that gamma irradiation is effective for coking wastewater treatment, not only for removing organic contaminants and TSS, but also for reducing pH value. The rate of removal for TSS and TOC is 81.43 and 95.22%, respectively, at the absorbed dose of 7 kGy. Irradiation of water by high γ-rays rays results in the formation of hydroxyl radical, ·OH, and the hydroxyl radical reacts strongly with most of the organic matters. The resulting free radicals further react with dissolved molecular oxygen to produce peroxy radicals, initiating a sequence of oxidative degradation reactions that may lead to the degradation and decomposition of organic pollution and solid particles in coking wastewater [20].

A number of investigations have reported that the COD decreased with the increasing of absorbed doses after gamma irradiation in wastewater [11,17,20]; but the results of this study showed that the COD decreased at the lower doses but increased at the higher doses, which was in accordance with the conclusion acquired from slaughterhouse wastewater [15]. The conflicting results may be attributed to the different pollutant compositions in coking wastewater. Overall, the COD could be reduced by gamma irradiation in coking wastewater, but further studies for the effective COD removal doses need to be performed.

The primary standard values of COD and TOC are 60 and 20 mg/L, respectively, and the secondary standard values of COD and TOC are 120 and 30 mg/L in the wastewater in China (GB8978-1996).The absorbed dose of 7 kGy is enough to remove the TOC in the coking sample in the study, in which wastewater treated by ^{60}Co-γ irradiation with 7 kGy could reach the primary standard for TOC. But the absorbed dose of 7 kGy is not enough for the treatment COD in the coking sample and it can be concluded that the method of ^{60}Co-γ irradiation combined with other treatment methods are more effective in removing COD than the direct irradiation methods.

The study stressed the advantages of using gamma radiation to remove organic contaminants of coking wastewater. It appears that gamma irradiation offer an alternative method to coking wastewater treatment that may have the extra benefit of improving the water quality.

Acknowledgments

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