KN-B removal from water by non-thermal plasma

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ABSTRACT

The degradation of Reactive Black 5 (KN-B) in water using double-dielectric barrier discharge (DDBD) was studied. Experimental results showed that the KN-B degradation rate increased as the initial pH decreased. Low concentrations of Fe²⁺ enhanced the degradation, whereas high concentrations of Fe²⁺ hindered the degradation. The results showed that DDBD did not noticeably reduce total organic carbon but did reduce the pH value and improve the biodegradability of the solution significantly. Furthermore, the UV–Vis spectra of the dye showed that the chromophore group was damaged and that the solution was decolorized after the 10-min degradation process.

INTRODUCTION

Azo dyes are the most widely used commercial reactive dyes used in dyeing processes, with a worldwide production of more than $7 \times 10^5$ tons per year (Fan et al. 2009; Gzmen et al. 2009). Most azo dyes are refractory organic chemicals. In wastewater, azo dyes cause chroma water problems and hinder the photosynthesis of aquatic plants, yet azo dyes are resistant to degradation by conventional wastewater treatment techniques, such as photolysis, oxidation, and biological treatment (Xue et al. 2008; Yu & Steven 2008; Zhou et al. 2009). Moreover, azo dyes are metabolism products of aromatic amines, which have mutagenic and carcinogenic properties (Marco et al. 2007). Owing to their non-biodegradability, toxicity and potential carcinogenic nature, the presence of azo dyes in wastewater has become a serious environmental problem. Thus, a new and efficient wastewater treatment technique for removing azo dyes from wastewater needs to be developed.

In recent decades, advanced oxidation processes (AOPs) have been proposed as an effective alternative for the treatment of refractory dye wastewater. Non-thermal plasma is a new advanced oxidation technology that has attracted the interest of scientists in recent years because of its unique advantages for the treatment of toxic and biorefractory organic pollutants (Shi et al. 2009; Tang et al. 2011). Pollutants are effectively removed by a variety of physical and chemical effects, such as high electric fields, ultraviolet photolysis, pyrolysis, and the formation of chemically active species such as radicals (•OH, •O) and molecules (H₂O₂, O₂, O₃) (Biljana et al. 2011; Zhu et al. 2010). Several non-thermal plasma methods for degrading dye pollutants, such as electron beam, glow discharge, pulsed corona discharge and dielectric barrier discharge (DBD), have been investigated (Liu et al. 2009; Monica et al. 2010; Yang et al. 2010). DBD is a non-equilibrium discharging process in which at least one dielectric layer is inserted in the discharging space to prevent current flow and release a large amount of plasma. Compared to other forms of discharge, DBD technology is especially suited for refractory wastewater treatment because of the stable, safe and higher energy characteristics of the discharge (Dong et al. 2008; Du et al. 2008; Zhang et al. 2010).

KN-B is a typical azo dye that is widely used in the textile industry; the research about ions produced during treatment and the pollutant degradation kinetics of the KN-B removal by double-dielectric barrier discharge (DDBD) has been investigated in our previous paper (Mei & Liu 2013). In this study, several factors affecting the degradation efficiency were studied in detail, and the removal mechanism was analyzed.

MATERIALS AND METHODS

Materials

All the chemicals used in this experiment are the same as described in Mei & Liu (2013): KN-B of 55% purity was
obtained from Sigma-Aldrich and used without any further purification. All of the other reagents, including sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), ferrous sulfate (FeSO₄·7H₂O), tert-butanol (C₄H₁₀O), potassium dichromate (K₂Cr₂O₇), ferrous ammonium sulfate ((NH₄)₂SO₄·FeSO₄·6H₂O) and phenanthroline (C₁₂H₈N₂·H₂O), were all analytical grade and were purchased from Sinopharm Chemical Reagent Co, Ltd. All solutions were prepared with deionized water with conductivity between 1.0 and 1.5 μS/cm.

Experimental process

The schematic diagram of the experimental setup was as shown in Mei & Liu (2013). The main equipment used to treat the KN-B solution was a quartz reaction tank, which consisted of two parts. The upper part of the reaction tank was slightly larger than the lower part. The lower part, which contained the solution, was 6 mm in height. The reaction tank was placed in the center of two aluminum electrodes. Power was supplied to the reactor by an AC source, which could be operated at an adjustable amplitude voltage. The intensity of discharge in the reaction tank depended on the input power, which was fixed at 60 W. The KN-B solution (100 mg/L) was prepared in deionized water. The initial solution conductivity was 91.9 μS/cm, and the pH was 5.30. For each run, 10 mL of solution was added to the reaction tank using a pipette. The gas above the water surface in the reaction tank was ambient air.

Analysis

KN-B degradation was monitored by measuring the maximum absorbance wavelengths in the visible region of the spectrum using a UV–Vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd, TU-1900). The detection wavelength was 600 nm with deionized water as the blank. The degradation efficiency for each sample was calculated using the following equation:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%$$

(1)

where $\eta$ is the degradation efficiency of KN-B (%), $C_t$ is the residual concentration of KN-B after the discharge treatment (mg/L), and $C_0$ is the initial concentration of KN-B before discharge treatment (mg/L).

UV–Vis absorption spectra of the aqueous solutions were measured before and after the plasma treatment by a spectrophotometer, in the wavelength range of 200–700 nm. The scanning width of the spectrophotometer was 1 nm.

The total organic carbon (TOC) content of the samples was determined using a Shimadzu TOC analyzer (model TOC-VCPH/CNP), and pH values were measured with a pH monitor (Shanghai LeiCi Instrument Co., Ltd, pHSJ-3F). All the experiments were run in duplicate, the experimental error was below 5%, and the average data were reported.

RESULTS AND DISCUSSION

Effect of pH on the degradation

Figure 1 shows the effect of pH on the degradation of KN-B. The buffer sodium bicarbonate was added to the solution to get a concentration of 1 mmol/L during the pH effect experiment. The curves indicated that the degradation efficiency was the highest under strongly acidic conditions (pH = 3.08), followed by neutral pH and alkaline pH. Biljana et al. obtained the same results in their experiments (Biljana et al. 2013). Degradation efficiency reached 99.5% after 10 min of treatment at pH 3.08. For the same discharge time and at initial pH values of 7.00 and 11.02, the degradation efficiencies were 97.0 and 92.3%, respectively.

The degradation rate may be affected by the pH in the following ways: carbonate species–HCO₃⁻ and CO₃²⁻ (from the mineralization of KN-B and buffer solution) existing in the solution are radical scavengers, which would result in a loss of hydroxyl radical activity (Reckhow et al. 1986). Additionally, the dissociation constants of H₂CO₃ are 6.37 and 10.33. Thus, at a pH of 11.02, carbonate exists in the form
of \( \text{CO}_3^{2-} \). Both carbonate and bicarbonate can scavenge hydroxyl radicals to generate less reactive species (\( \text{CO}_3^{2-} \) or \( \text{HCO}_3^- \)), which are more selective toward organic chemicals compared with \( \text{OH}^- \); consequently, the pollutant removal efficiency is reduced (Vione et al. 2009). When the initial pH is 7.00, carbonate coexists as \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \). For \( \text{CO}_3^{2-} \), the constant for the reaction rate with hydroxyl radical is \( 1.5 \times 10^7 \text{ L/(mol·s)} \), while for \( \text{CO}_3^{2-} \), the constant is \( 4.2 \times 10^8 \text{ L/(mol·s)} \). \( \text{HCO}_3^- \) has a weaker ability to consume hydroxyl radical than \( \text{CO}_3^{2-} \) under the same concentration. On the other hand, organic acids are generated in the discharge degradation process, which would further reduce the pH value, forcing some \( \text{HCO}_3^- \) to be converted into \( \text{H}_2\text{CO}_3 \) and thus contributing to the degradation of KN-B.

When the pH is less than 6.37, carbonate mainly exists in the form of carbon dioxide molecules. In this form, fewer radical scavengers are present, and thus, more hydroxyl radicals exist in the solution. Therefore, in this study, the degradation efficiency was the highest at the initial pH value of 3.08.

**Effect of adding Fe\(^{2+}\) on the degradation**

\( \text{H}_2\text{O}_2 \) was produced in large amounts during the discharge process (Locke & Shih 2011), and the pH decreased to about 3.00. The optimum pH value for the Fenton reaction is 2.8, so adding Fe\(^{2+}\) produces hydroxyl radicals through a Fenton reaction (1) (Li et al. 2011). The effect of adding Fe\(^{2+}\) on the degradation of KN-B was studied with 60 W of input power (Figure 2). The initial pH was 5.30, and the initial concentration of KN-B was 100 mg/L.

It was evident that the degradation efficiency increased with the Fe\(^{2+}\) concentration in the range of 0.25–1.00 mmol/L, while the opposite trend was observed for higher concentrations of Fe\(^{2+}\) (2.00 mmol/L). The curves also indicated that the degradation efficiency of KN-B was the highest at a Fe\(^{2+}\) concentration of 1.00 mmol/L.

Low concentrations of Fe\(^{2+}\) may have enhanced the degradation of KN-B because the \( \text{H}_2\text{O}_2 \) formed in the DDBD conditions greater than the amount of Fe\(^{2+}\), so a good degradation could be obtained. Continually increasing of the concentration of Fe\(^{2+}\) led to less \( \text{H}_2\text{O}_2 \) accumulation in the reaction medium and less efficient formation of \( \cdot \text{OH} \). Excess Fe\(^{2+}\) reacted with \( \cdot \text{OH} \), which could be explained by the reaction below (2, 3) (Li et al. 2011). Because Fe\(^{3+}\) is less oxidative compared to \( \cdot \text{OH} \), higher concentrations of Fe\(^{2+}\) would hinder the degradation:

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \cdot \text{OH} + \text{OH}^- + \text{Fe}^{3+} \quad (2) \\
\text{Fe}^{2+} + \cdot \text{OH} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (3)
\end{align*}
\]

**UV–Vis before and after degradation**

The UV–Vis spectrum of the KN-B solution during the discharge was studied with an input voltage of 65 V, input power of 60 W, initial pH of 5.30 and initial KN-B concentration. Samples were taken after 0, 2, 4, 6, 8, and 10 min during the discharge process (Figure 3).
As shown in Figure 4, there are four characteristic absorption peaks. The absorption peak of KN-B is at 600 nm, the absorption peak of the naphthalene ring is at 312 nm, the absorption peak of the benzene ring is at 254 nm, and a conjugated system formed by the benzene ring, naphthalene ring and azo bond absorption peak is at 390 nm (Panizza & Cerisola 2009). The absorbance at 600 nm decreased during the experiment, and the absorption peak completely disappeared after 10 min, which corresponds to the decolorization of the KN-B solution and could be explained by the breaking down of the azo group. However, the absorption peaks at 254 and 390 nm did not completely disappear, meaning that the ring structures of naphthalene and benzene was not completely destroyed after 10 min. The average bond dissociation energy is 109 kJ/mol for an azo bond (Standard bond energies), 418–628 kJ/mol for a benzene ring, and greater than 628 kJ/mol for a naphthalene ring (Reaction thermochemistry data). It should be noted that there was still strong absorption in the range of 200–230 nm, possibly from the small-molecule intermediates.

Infrared (IR) spectrum before and after degradation

To understand the degradation mechanism of KN-B clearly, the IR spectra before and after 10 min of degradation were studied. The results are shown in Figure 4. The curves indicate that there was a significant change as a result of the dye degradation. An amino stretching vibration absorption peak was observed at 3,170 cm\(^{-1}\), which might be the amino structure generated by the fracturing of the azo bond. The peaks of naphthalene increased from 1,590 to 1,670 cm\(^{-1}\), and the absorption intensity decreased, indicating that the naphthalene ring's main structure was destroyed. The absorption peak at 1,450 cm\(^{-1}\) is the stretching vibration of the benzene ring, indicating that the benzene ring was not destroyed completely. The disappearance of the absorption peak at 1,490 cm\(^{-1}\), combined with the complete decolorization of KN-B, resulted from the destruction of the azo bond structure. The absorption peak at 1,060 cm\(^{-1}\) is the C–O stretching vibration of carboxylic acid or ester, indicating that KN-B was oxidized to carboxylic acids or esters.

Therefore, during the process of KN-B degradation using DDBD, the azo bond is destroyed first, followed by the benzene ring structure and the naphthalene ring structure. This process also produced small molecule acids. These results are consistent with the UV–Vis spectroscopy results.

TOC and pH changes during experiment

TOC did not change greatly during the whole experiment: the TOC removal efficiency was only 15.4% after 10-min treatment. This result further confirmed that the dye was converted into organic intermediates, which still existed in the aqueous solution. The pH value decreased significantly during the experiment, decreasing most rapidly in the first 2 min to below 3.0 and then gradually reducing further to about 2.0 after 10 min. The drop in pH may have resulted from the generation of organic and inorganic acids, such as nitric and nitrous acids, from the discharge induced reactions of N\(_2\) with H\(_2\)O (Burlica 2006; Spataru 2004).

Biodegradability change after DDBD treatment

Although the TOC value did not reduce effectively, the biodegradability of KN-B was significantly enhanced after treatment, based on the increased biochemical oxygen demand/chemical oxygen demand (BOD\(_5\)/COD) value from 0.08 to 0.5. These data proved that the KN-B molecule was deconstructed, but no efficient mineralization occurred in the reaction. As shown in the IR spectra (Figure 4), KN-B was oxidized to carboxylic acids or esters; these byproducts have higher biodegradability.

CONCLUSION

DDBD removed KN-B effectively. The degradation rate of KN-B increased as the initial pH decreased. Fe\(^{2+}\) enhanced the degradation at low concentrations but hindered
degradability of KN-B was greatly increased after treatment. That the aromatic ring of KN-B was degraded partly. The biodegradability of KN-B was greatly increased after treatment.

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