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Ultrasonics Sonochemistry

Sonochemical degradation of naphthol blue black in water: Effect of operating parameters

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A B S T R A C T

In this work, the sonochemical degradation of naphthol blue black (NBB), an acidic diazo dye, in water was investigated. The effects of several operating parameters such as initial NBB concentration, acoustic intensity, ultrasonic frequency, nature of the dissolved gas and solution pH on the degradation of the dye were carried out. The obtained results showed that ultrasound completely destroyed NBB ($5\,mg\,L^{-1}$) after 45 min of sonication and most of the chemical oxygen demand was eliminated after 90 min of treatment. It was found that the initial rate of sonolytic degradation increased with increasing the initial NBB concentration. The fitting of the experimental data by a heterogeneous Langmuir-kinetics model showed that NBB degraded mainly at the interfacial region of the bubble by hydroxyl radical ($^{\cdot}OH$) attack. The degradation rate of the dye increased substantially with increasing acoustic intensity in the range of 0.44–$3.58\,W\,cm^{-2}$ and decreased with increasing frequency in the range of 585–1140 kHz. The rate of NBB degradation decreased in the order of Ar > air > N_2. The significant degradation was achieved in acidic conditions (pH 2) where the initial degradation rate was 1.37 and 1.66 higher than those observed at pH 6 and pH 10, respectively.

1. Introduction

Wastewater from textile industry impose serious environmental problems, because of their color and their potential toxicity [1,2]. The release of colored wastewaters in the ecosystem is a dramatic source of aesthetic pollution and perturbations in aquatic life [3]. Dye pollutants in wastewaters are the principal source of environmental aqueous contamination. Their removal from water is thus ecologically necessary to offer a cleaner environment as a requirement for human health and has attracted the most wanted attention of environmentalists, technologists and entrepreneurs. Approximately half of all known dyes are azo dyes, making them the largest group of synthetic colorants [4]. These chemicals present a potential human health risk as some of them have been shown to be carcinogenic [4]. A variety of physical, chemical and biological methods are presently available for the treatment of wastewater discharged from various industries. Conventional methods of the treatment of dye wastewater include adsorption [5], chlorination and ozonation [6,7], electrochemical methods [8,9], biological methods [10,11], chemical oxidation [12,13]. Many advanced oxidation processes (AOPs) were also used for the oxidation of dyes in water [14,15]. These techniques (AOPs), which involve an in situ generation of highly oxidizing agents such as $^{\cdot}OH$ radical, have emerged as an important class of technologies to accelerate the non-selective oxidation.

Over the past two decades, sonochemical degradation of organic pollutants in water has been extensively investigated as a novel AOPs [16–20]. The chemical effects of sonication arise from acoustic cavitation, namely the formation, growth, and implosive collapse of bubbles in a liquid, which produces unusual chemical and physical environments [21]. The collapse of the bubbles induces localized extreme conditions. It has been reported that the gaseous contents of a collapsing cavity reach temperatures as high as 5200 K and pressures higher than 500 atm, and about 1900 K in the interfacial region between the solution and the collapsing bubble [22]. Under such conditions, molecules trapped in the bubble (water vapor, gases and vaporized solutes) can be brought to an excited-state and dissociate [23]. As a result, reactive species such as $^{\cdot}OH$, $HO_2^{\cdot}$, $H^{\cdot}$ and O are created from H_2O and O_2 dissociation and their associate reactions in the bubble [23]. These active species can recombine, react with other gaseous species
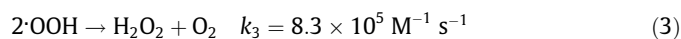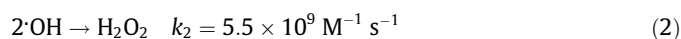
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present in the cavity or diffuse out of the bubble into the bulk liquid medium where they are able to induce chemical transformation [23]. In this situation, if organic pollutants exist in the liquid phase, they will react according to their physico-chemical properties: volatile substrates will be pyrolyzed in the bubble by the high core temperature whereas non-volatile substrates will be oxidized by hydroxyl radicals at the bubble–liquid interface and in the bulk liquid solution (Reaction 1) [24].

$$S + \cdot OH \xrightarrow{k_1} \cdot SOH \rightarrow Products \tag{1}$$

In the absence of any solutes in the liquid medium, these primary active species of sonolysis mostly recombine at the bubble solution interface to form hydrogen peroxide (H_2O_2) that is released in the medium according to the following reactions [25]:

$$2 \cdot OH \rightarrow H_2O_2 \quad k_2 = 5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \tag{2}$$

$$2 \cdot OOH \rightarrow H_2O_2 + O_2 \quad k_3 = 8.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \tag{3}$$

Due to their high reactivity and their short lifetime, the total number of primary active species produced by the acoustic bubbles cannot be directly measured. It is generally accepted that the yield of H_2O_2 can be considered as an indicator for quantifying the overall chemical yield of ultrasound in aqueous medium [26,27].

In the present work, an anionic diazo dye, naphthol blue black (NBB), was chosen as a model substrate for a systematic study of the sonochemical degradation process. Naphthol blue black is an industrially important acidic diazo dye, which has a high photo- and thermal stability [4]. It is widely used in the textile industry for dyeing wool, nylon, silk and textile printing [4]. Other industrial use includes coloring of soaps, anodized aluminum and casein, wood stains and writing ink preparation [4]. The objective of this study was to assess the potentiality of ultrasound to remove NBB from water and to evaluate the effects of some parameters on the sonodegradation process.

2. Materials and methods

2.1. Reagents

Naphthol blue black (abbreviation: NBB; Acid Black 1; C.I. number: 1064-48-8; chemical class: azo dye; molecular formula: $C_{22}H_{14}N_6Na_2O_9S_2$, molecular weight: 616.49 g mol^{-1}) was supplied by Sigma–Aldrich and used without any purification. The molecular structure of NBB was shown in Fig. 1.

Potassium iodide (KI) was supplied by Riedel-de Haën. Ammonium heptamolybdate $(NH_4)_6Mo_7 \cdot 4H_2O$ and sodium hydroxide (NaOH) were procured from Sigma–Aldrich. Silver sulfate (Ag_2SO_4), potassium dichromate ($K_2Cr_2O_7$) and sulfuric acid (H_2SO_4) were supplied by Acros Organics.

2.2. Ultrasonic reactor

Sonolysis experiments were conducted in a cylindrical water-jacketed glass reactor of a total volume of 500 mL. The ultrasonic waves of 585, 860 and 1140 kHz were delivered from the bottom
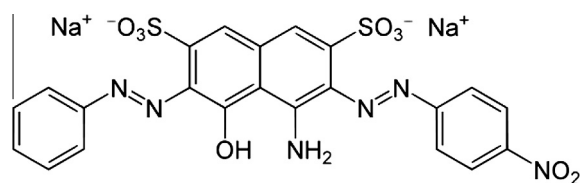

Fig. 1. Molecular structure of NBB.

through a Meinhardt multifrequency transducer (model E/805/T/M, diameter of the active area 5.3 cm). The temperature of the solution was monitored using a thermocouple immersed in the reacting medium. Acoustic power dissipated in the reactor was estimated using a standard calorimetric method [28,29]. The range of acoustic power used in this study was from 9.7 to 79 W.

2.3. Procedures

All NBB solutions were prepared with distilled water. Sonochemical experiments involving NBB degradation and H_2O_2 production in pure water were carried out under different conditions using constant solution volume of 300 mL. The pH of the solution was adjusted using NaOH or H_2SO_4. Aqueous samples were taken periodically from the solution and the concentrations of the dye were determined using a UV–visible spectrophotometer (Lightwave II) at 620 nm. The temperature of the sonicated solution was kept at 25 °C by circulating cooling water through a jacket surrounding the cell. In the tests conducted to investigate the effects of different dissolved gases, a gas cylinder was used for bubbling Ar, air or N_2 at least 15 min prior to start and until completion of experiments. In all the other experiments, the reactor was open to the air without any saturation (control conditions).

Hydrogen peroxide concentrations in water were analytically determined using the iodometric method [30]. Sample aliquots taken periodically from the reactor during sonolysis were added in the quartz cell of the spectrophotometer containing 1 mL of potassium iodide (0.1 M) and 20 μL of ammonium heptamolybdate (0.01 M). The iodide ion (I^-) reacts with H_2O_2 to form the triiodide ion (I_3^-). The mixed solutions were allowed to stand for 5 min before absorbance was measured. The absorbance was recorded with a UV–visible spectrophotometer (Lightwave II) at the maximum wavelength of the formed triiodide (I_3^-) (352 nm; the molar absorptivity ϵ = 26,300 L mol^{-1} cm^{-1}).

Chemical oxygen demand (COD) was measured according to the method presented by Thomas and Mazas [31], using a dichromate solution as the oxidizer in a strong acid medium. Test solution (2 mL) was transferred into the dichromate reagent and digested at 150 °C for 2 h. The optical density for the color change of dichromate solution was determined with a spectrophotometer at 440 nm.

3. Results and discussion

3.1. Characterization of NBB sonolysis

The ultrasonic treatment of 5 mg L^{-1} of NBB solution caused a substantial decrease of the band located at 620 nm (color decay) within 45 min of sonication. The NBB concentration decreased exponentially with time (Fig. 2), agreeing with the results of Stock et al. [32] observed at 640 kHz. Besides the degradation process, the ultrasonic treatment resulted in the formation of hydrogen peroxide (Reactions (2) and (3)), which can be used to estimate the amount of ·OH radicals released by the bubbles at determined sonochemical conditions as $k_2 \gg k_3$. In absence of substrate, the concentration of H_2O_2 increased linearly with sonication time (Fig. 2). As mentioned above, the two major pathways for the sonochemical degradation of organic compounds in dilute aqueous solution are: (i) thermal decomposition of volatile pollutant molecules entrapped inside the bubble and (ii) the reaction of ·OH radicals with the solute at the bubble interface and in the bulk solution [23,24]. NBB is a non-volatile compound (Henry's law constant: 1.2×10^{-31} atm m^3 mol^{-1}, vapor pressure: 4.8×10^{-29} mm Hg at 25 °C, solubility: >100 g L^{-1}) [33]; consequently, it cannot enter the bubble but must be eliminated through reaction with hydroxyl