



Degradation of azo dye acid red B on manganese dioxide in the absence and presence of ultrasonic irradiation

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Abstract

Degradation of azo dye acid red B (ARB) on MnO_2 in the absence and presence of ultrasonic irradiation (sonication) has been investigated. The effect of initial pH, anions (Cl^- , NO_3^- , SO_4^{2-}), and saturated gas (argon/oxygen) has been studied. The experimental results show that decolorization of the dye on MnO_2 is highly pH dependent, with increasing decolorization efficiencies at decreasing pH values. The SO_4^{2-} and NO_3^- ions are observed to suppress the adsorption of ARB on MnO_2 dramatically, suggesting competitive nature with the dye. Sonication accelerates decolorization and mineralization of the dye. And oxygen used as saturated gas is more favorable for mineralization of the dye than argon. The average particle diameter of MnO_2 decreases from 47.5 to 3.19 μm after sonication.

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1. Introduction

Azo dyes constitute the largest class of dyes used in industry. In the textile industry, it is estimated that 10–15% of the dye is lost during the dyeing process and released as effluent. Azo dyes are resistant to aerobic degradation; however, under anaerobic conditions, the azo linkage is reduced to generate aromatic amines that are colorless but can also be toxic and potentially carcinogenic.

The conventional treatment methods for eliminating dyes from the waste stream include flocculation with lime, activated charcoal adsorption, and biotreatment. Lime treatment and

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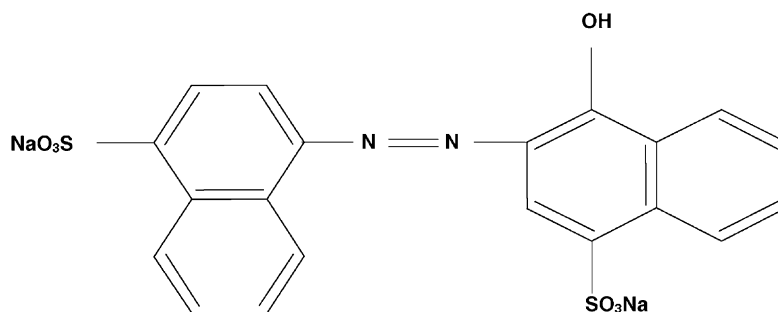
charcoal adsorption generate large amount of solid wastes, which require costly disposal and regeneration methods. Biotreatment processes rely on indigenous soil microorganisms to degrade dye compounds. Since the synthetic dyes are resistant to aerobic biodegradation, this process is likely to be insufficient. Thus, there is a need for developing treatment technologies that are more effective in eliminating dyes from the waste stream at its source.

Advanced oxidation processes (AOPs), based on the chemical, photochemical and photocatalytic production of hydroxyl radicals ($\bullet\text{OH}$), which act as strong oxidizing agents, have emerged as a promising technology for the degradation of organic pollutants. The methods for generating hydroxyl radicals are diverse, ranging from homogeneous oxidation such as $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ [1] and UV/O_3 [2] to heterogeneous photocatalysis involving illumination of large bandgap semiconductor particulates either dispersed in slurries or immobilized on films [3,4]. While photocatalysis has been studied extensively, its commercialization has yet not been realized and barriers prevail [5–7]. Additionally, there is some interest in on-stream ozonation and chlorination treatment processes, environmental problems associated with both chlorine and ozone render both unattractive.

Sonochemical degradation of organic pollutants has received increasing attention in recent years [8–14]. The chemical effects of high-intensity ultrasound result primarily from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in liquids [15]. Acoustic cavitation generates sites of locally high temperatures and pressures for short period of time, which give rise to the H_2O sonolysis with production of radical species ($\text{H}\bullet$, $\bullet\text{OH}$, $\text{HOO}\bullet$) and direct destruction of solute [9,16,17]. However, little information is available on heterogeneous sonochemical degradation of organic pollutants.

Manganese oxides exhibit considerable activity in oxidation–reduction reactions due to the presence of manganese ions with different oxidation states. Unfortunately, it has been shown that manganese oxides are insoluble [18,19]. However, the amount of manganese dissolved in solution can be increased considerably in acidic medium with the addition of organic compounds such as dyes [20]. But the further adsorption and oxidation of dye compound on the mineral particles interface reduce their surface areas and lead to inhibition of the process [21].

In this work, decolorization of azo dye acid red B (ARB) in the absence and presence of ultrasound is investigated. The motivation of this work is to investigate the feasibility of degradation organic pollutants in heterogeneous sonochemical reactions.



2. Materials and methods

2.1. Materials

Manganese dioxide of analytical reagent grade was supplied by Shanghai Chemical Reagents Company. Acid red B was purchased from Beijing Qinghe Knitting Mill and used without further purification. Stock solution (2000 mg/l) of the dye was prepared with deionized water, and further diluted to various concentrations in the experiment. All the other chemicals used in this study were of analytical reagent grade. Argon and oxygen gases were of purity >99.99%.

2.2. Analyses

The surface area of MnO₂ was determined by Brunauer–Emmett–Teller measurements (BET) using nitrogen gas and a multipoint method on a Micromeritics accelerated surface area and porosimetry (ASAP) 2000. The surface area of the MnO₂ is 29.3 m²/g. The particle size of MnO₂ in the suspension was recorded on a Mastersizer 2000 Laser Particle Analyzer (Malven).

The aliquots were collected at timed intervals and filtrated through a 0.2 μm syringe-end filter. The concentration of the dye in the filtrate was determined using UV-Vis Spectrophotometer (Hitachi Model 3010) at 515 nm. Total organic carbon (TOC) measurements were performed on a Shimadzu TOC Analyzer Model 500. Dissolved manganese was determined on a Hitachi Model Z-6100 atomic absorption spectrophotometer. The zeta potential was recorded on a Zetasizer Model 2000 (Malven).

2.3. Experimental procedures

Decolorization experiments of ARB on MnO₂ in the absence of ultrasonic irradiation were carried out in batch mode. A 100 ml volume of dye solution, previously adjusted to a fixed pH value with diluted NaOH and HCl, HNO₃ or H₂SO₄, respectively, was added to a 250 ml beaker containing different amount of MnO₂. The suspensions were immediately shaken in an air-bath (25 ± 1 °C, 150 rpm) (Model HZQ-C) for 4 h.

The sonochemical experiments were carried out in a Branson S3200 (50 kHz, 150 W) ultrasonic cleaning bath. Thermostating was done using coolant passed through copper coils (outer diameter 6 mm) suspending in the bath connected with a thermostat. The temperature of the bath was kept at ~22 °C. A 250 ml conical glass reactor with a plane bottom of thin glass in order to minimize sonic absorption and to ensure good heat exchange with the water bath was fitted at a constant position. The initial concentration of ARB was 100 mg/l and the volume exposed to sonication was 100 ml. The pH of the solution was adjusted to 3.0 with diluted NaOH and H₂SO₄. The suspension was stirred with a mechanical stirrer to ensure good liquid–solid mass transfer. At timed intervals, 5 ml of suspension was withdrawn with a syringe. Then the sample was immediately filtrated through a 0.2 μm filter for analysis of absorbance, dissolved manganese and TOC. The control experiment was performed without sonication under argon atmosphere; other experimental conditions were the same as above.

During the entire process, pH was not readjusted and no buffer solution was used.

3. Results and discussion

The dye effluents are generally characteristic of strong pH and anions variations. The pH, which results in modification of the physical properties (including charge) of molecules with ionisable functional groups, plays an important role in the adsorption and oxidation of ARB on MnO_2 . Therefore, both pH and anions were chosen as the main factors in the present study.

3.1. Effect of pH on the decolorization of ARB in the absence of sonication

The decolorization efficiency of ARB on MnO_2 in the absence of ultrasound irradiation at different pH levels was shown in Fig. 1. The pH of the solution was adjusted with diluted NaOH and HCl. It was found that the decolorization of the dye over MnO_2 was highly pH dependent, with the decolorization efficiencies increased with decreasing pH values. At pH > 10, the decolorization of the dye was negligible. Both the surface charge of MnO_2 and the solution speciation of ARB (H_2L) changed with pH. Protonation of the oxide surface and azo dye as a function of pH may be represented as follows:

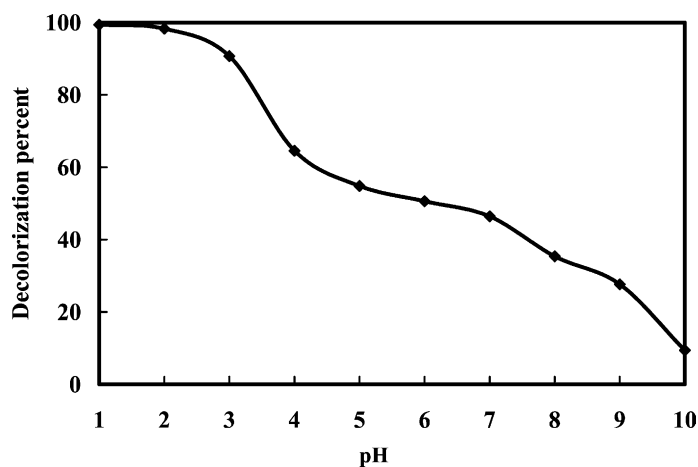
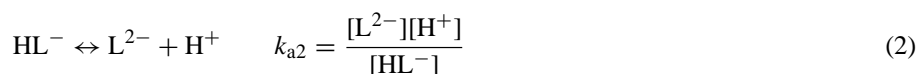
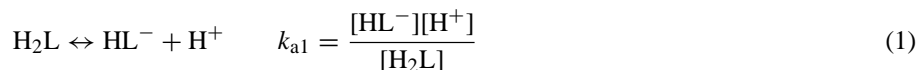
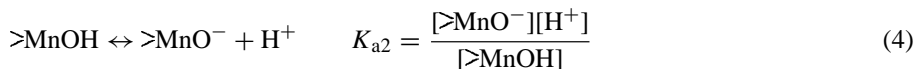
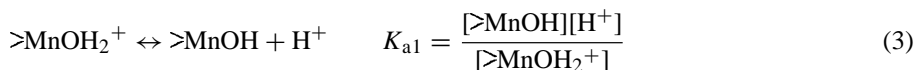
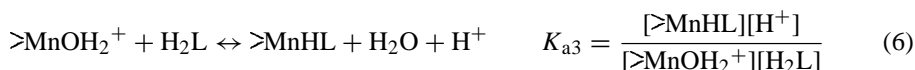
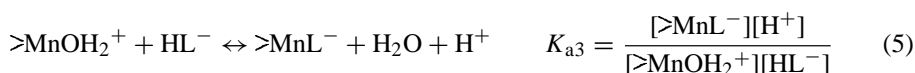


Fig. 1. Effect of pH on ARB adsorption on MnO_2 (2 g/l) in the absence of sonication, initial pH adjusted to 3.0 with diluted NaOH and HCl.



The oxidation of organic compounds on manganese oxide may be described involving the diffusion of organic compound to the particle surface to first form a complex, followed by exchange of electrons with the reactive surface of MnO_2 [22]. For ARB, as a hydrophilic substrate, the neutral species more easily diffuse to and accumulate at the surface of MnO_2 in comparison with its corresponding ionic forms. The decolorization efficiency remarkably increased as the pH decreased from 4 to 3. One possible explanation is that the reaction due to electrostatic attraction between the predominant protonation level species HL^- and MnOH_2^+ readily takes place in this pH range as follows:



The zeta potential profile of the ARB/ MnO_2 suspension shown in Fig. 2 may further prove the above explanation to some extent. The fluctuation of decolorization occurred near pH 3, where is the point of zero charge (PZC) of MnO_2 [23]. Hence, the oxidizing ability of MnO_2 can be sharply enhanced [22].

3.2. Effect of anions on the decolorization of ARB in the absence of sonication

It was very interesting to find out in this study that counteranions such as Cl^- , NO_3^- and SO_4^{2-} , even at very low concentrations, strongly affected the decolorization of ARB on MnO_2 , especially at high ARB concentrations (Fig. 3). In these cases, solutions of different

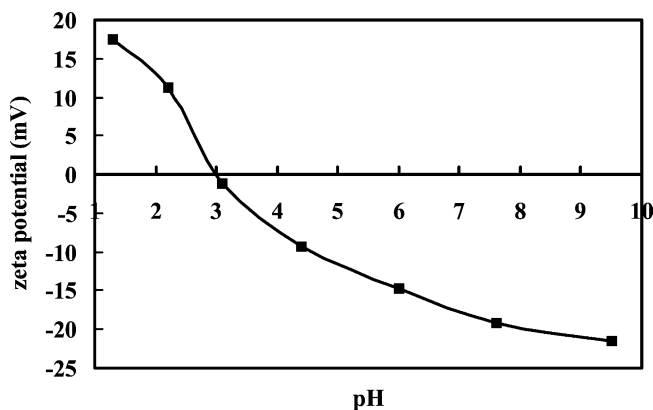


Fig. 2. Zeta potential of ARB/ MnO_2 as a function of solution pH.

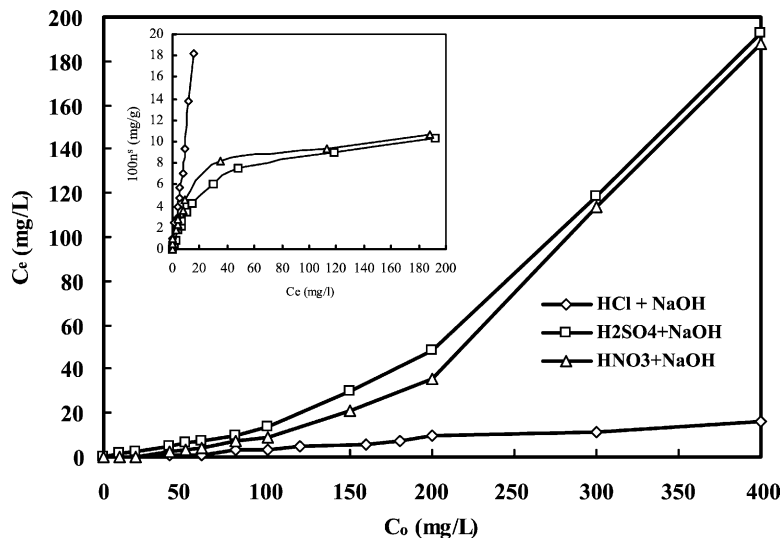


Fig. 3. Effect of anions on the decolorization of ARB by 2 g/l MnO_2 at pH = 3.

ARB concentrations were adjusted to pH 3 with diluted NaOH and HCl, HNO₃ or H₂SO₄, respectively. The extent of the adsorption was calculated as follows:

$$n^s = \frac{(C_0 - C_e)V}{W} \quad (7)$$

where n^s is the adsorbed amount (mg/g), C_0 the initial concentration, C_e the final concentration, V the volume, and W is the weight of MnO_2 .

The adsorption of ARB on MnO_2 decreased dramatically when SO_4^{2-} or NO_3^- was added in solution along with the azo dye, indicating the competitive nature of these anions with the dye during the adsorption process, suggesting that the sulfonic group of ARB may be the binding site for this dye on MnO_2 .

3.3. Decolorization and mineralization of ARB on MnO_2 in the presence of ultrasonic irradiation

The decolorization and mineralization of ARB in the presence of ultrasonic irradiation are shown in Figs. 4 and 5 (US for ultrasonic irradiation), respectively. It was apparent, as shown in Fig. 4, that the decolorization efficiency on MnO_2 was much higher in the presence of ultrasonic irradiation. The decolorization efficiency was increased from 77.03 (MnO_2 alone, control) to 90.88 (oxygen atmosphere) and 94.93% (argon atmosphere), respectively. Fig. 5 showed that the TOC removal after 240 min was 11.89 (control), 48.12 (oxygen atmosphere) and 29.11% (argon atmosphere), respectively. It was clearly shown that oxygen used as saturated gas was more favorable for mineralization of the dye than argon. However, almost no decolorization of the dye was found when it was exposed to ultrasonic irradiation alone.

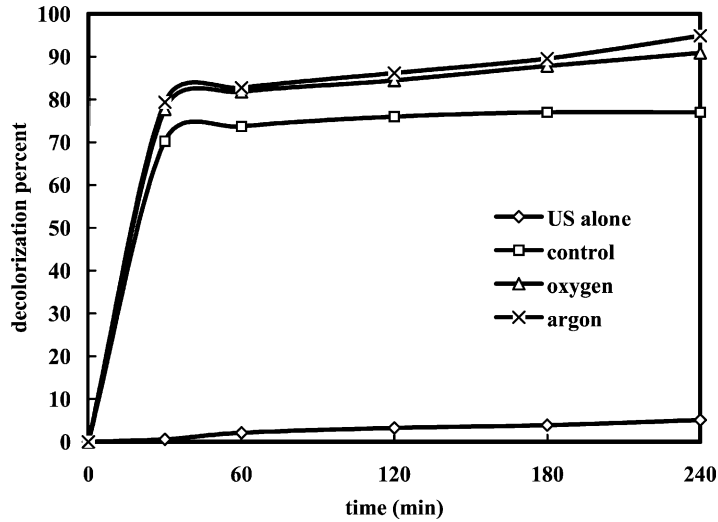


Fig. 4. Decolorization of ARB by 1 g/l MnO₂ at initial pH = 3 adjusted with diluted NaOH and H₂SO₄.

Firstly, colloidal MnO₂ was readily formed during ultrasonic irradiation, which enhanced mass transfer. The average particle diameter of MnO₂ was reduced from 47.5 to 3.2 μm after 240 min ultrasonic irradiation of the dye–MnO₂ suspension (Fig. 6). A rough calculation for increase in surface area due to decreased particle size can be made as follows.

Assumed that adsorbent particles are spheres, for a single sphere:

$$S = \text{surface area} = \pi d^2$$

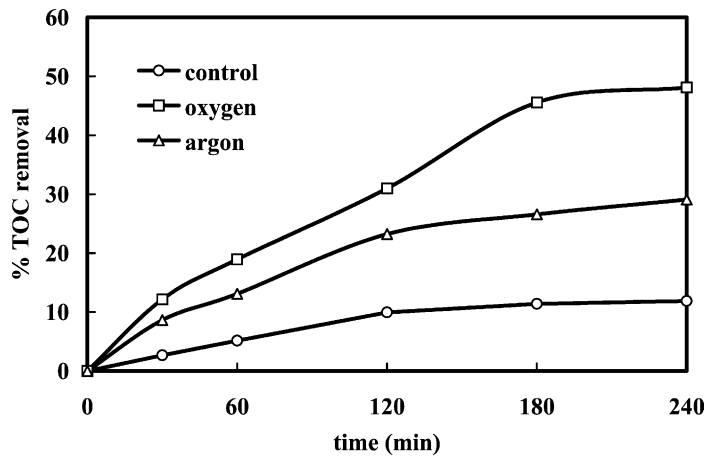


Fig. 5. TOC removal as a function of time at initial pH = 3 adjusted with diluted NaOH and H₂SO₄, MnO₂ added amount 1 g/l.

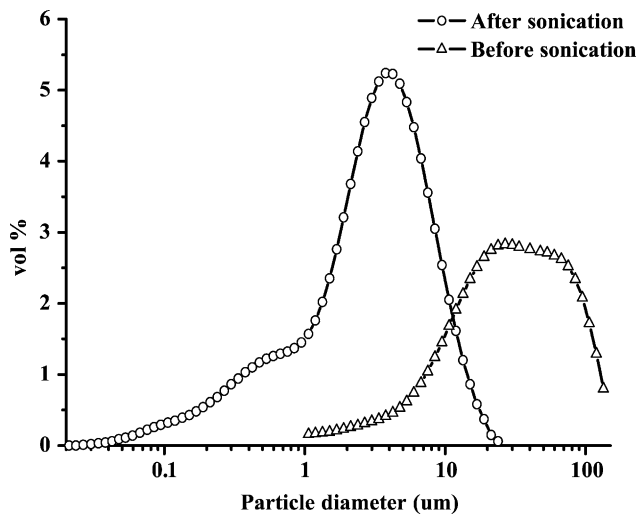


Fig. 6. Particle size reduction of MnO_2 after 240-min sonication at initial pH = 3 adjusted with NaOH and H_2SO_4 .

$$V = \text{volume} = \frac{1}{6}\pi d^3$$

$$a = \text{specific surface area} = \frac{S}{V} = \frac{6}{d}$$

Thus, increase in surface area can be estimated as (assuming the mass of particles remains the same)

$$S_{\text{ratio}} = \frac{a_{\text{after sonication}}}{a_{\text{before sonication}}} = \frac{d_{\text{before sonication}}}{d_{\text{after sonication}}} = \frac{47.5 \mu\text{m}}{3.2 \mu\text{m}} = 14.84$$

Since adsorption depends on available surface area, the adsorption capacity of ARB over MnO_2 would be enhanced due to the increase of the surface area with reduced particle size for a given mass of MnO_2 particles.

Secondly, ultrasonic irradiation accelerated heterogeneous reactions due to removal of the passivating outer oxide layer normally present on MnO_2 surfaces via its microjetting effects [24,25]. Therefore, the inhibition of adsorption and oxidation of dye compound on MnO_2 surface is greatly alleviated.

Most important, H_2O_2 is produced during sonication of water [26,27], which enhances the dissolution of MnO_2 and replenishes the particle surface with fresh MnO_2 surfaces. The dissolution rate of manganese dioxide was enhanced as shown in Fig. 7. As indicated in Fig. 7, the dissolution of manganese dioxide increased greatly in the presence of sonication, especially with argon as saturated gas. The physical phenomena leading to sonochemical effects in water are complex and not yet fully elucidated. Nevertheless, whatever the theoretical model describing the origins of the molecular activation (thermal and/or electrical), the molecules are brought to an excited state and dissociate in the interior of the bubble of

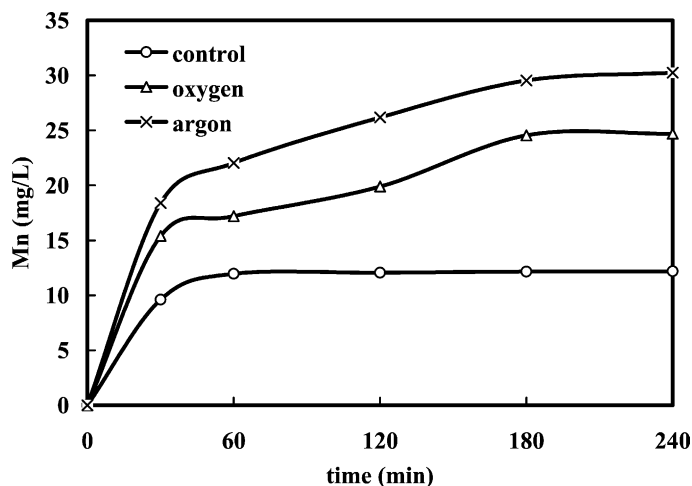


Fig. 7. Dissolution of manganese with reaction time at initial pH = 3 adjusted with NaOH and H₂SO₄, MnO₂ added amount 1 g/l.

cavitation, which is filled with gas and vapor. The first step appears to be the cleavage of water resulting in the formation of hydroxyl and hydrogen radicals.



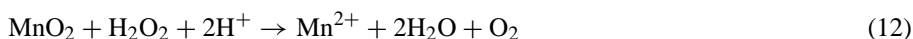
In the presence of oxygen, no hydrogen is formed. This is explained by the scavenging of H atoms by O₂ in the gas bubbles [27]:



The processes that lead to the formation of H₂O₂ include [16,26]:



With MnO₂ present, the following reactions can be expected to occur:



In the presence of argon at low acoustic frequency, the hydrogen peroxide formation rate is higher [28,29], while more hydroxyl radicals are produced if the solution is saturated with oxygen [16]. Hence, more $\bullet\text{OH}$ is scavenged by both H₂O₂ and H to form H₂O with argon as saturated gas, which was not favorable for mineralization of the dye as compared with oxygen. It should also be pointed out that $\bullet\text{OH}$ could be scavenged by excess amount of Mn²⁺, which needs further investigation to find out the optimum amount of MnO₂ needed in the future work.

4. Conclusion

The decolorization of azo dye ARB on manganese dioxide in the absence/presence of ultrasonic irradiation has been studied. The decolorization process is highly pH dependent, with increased efficiency at decreasing pH values. Counteranions such as SO_4^{2-} and NO_3^- greatly inhibit the decolorization process, indicating the competitive nature of these anions with the dye during the adsorption process. The decolorization efficiency is much higher in the presence of ultrasonic irradiation than using MnO_2 alone. Moreover, oxygen used as saturated gas is more favorable for mineralization of the dye. It is feasible to incorporate ultrasonic irradiation and MnO_2 for degradation of azo dyes, both for decolorization and mineralization of the dye. Given the acidic nature of the final solution, some form of the neutralization would probably be necessary before eventual discharge.

Acknowledgements

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