Chemical coagulation and sonolysis for total aromatic amines removal from anaerobically pre-treated textile wastewater: A comparative study

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Abstract. The present study primarily focuses on the evaluation of the comparative effect of chemical coagulation and ultrasonication for elimination of aromatic amines (AAs) present in anaerobically pretreated textile wastewater containing different types of dyes including azo dyes. Color and COD reduction was also monitored at the optimized conditions. The production of AAs was measured spectrophotometrically in the form of total aromatic amines (TAAs) and also verified with high performance liquid chromatography (HPLC) selectively. A composite coagulant, magnesium chloride (MC) aided with aluminium chlorohydrate (ACH) in an equal ratio (MC + ACH) was utilized during the coagulation process, which yielded 31% of TAAs removal along with 85% of color and 52% of COD reduction. At optimized power (200 W) and sonication time (5 h), an appreciable TAAs degradation efficiency (85%) was observed along with 51% color reduction and 62% COD removal using ultrasonication. The chromatographic data indicate that sulphanilic acid and benzidine types of aromatic amines were produced after the reductive cleavage of utilized textile dyes, which were effectively mineralized after ultrasonication. The degradation followed the first order kinetics with a correlation coefficient (R^2) of 0.89 and a first-order kinetic constant (k) of 0.0073 min^{-1}.

Keywords: aromatic amines degradation; chemical coagulation; UASB reactor effluent; textile dyes; ultrasonication

1. Introduction

Textile industries are rapidly increasing to meet the necessities of the growing population and to contribute to the economy of the nation. However, effluents from the textile industries are one of the major sources of environmental pollution and public health concerns, particularly in many urban areas. These effluents are heavily polluted with the complex organic and inorganic
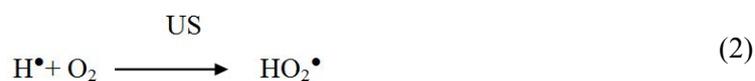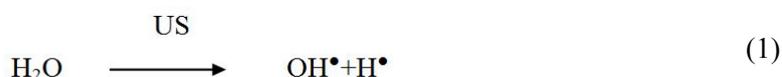

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chemicals which are used during various steps of textile processing and the unused materials from each process are discharged as wastewater. The effluents from the textile industry possess high biological oxygen demand (BOD), chemical oxygen demand (COD), turbidity, pH, toxic chemicals and strong color due to the presence of residual dyes. The presence of a very small concentration of residual dye in water is highly visible and therefore, affects the receiving environment not only aesthetically, but also disturbs the aquatic life by obstructing the light penetration and oxygen transfer. During textile processing, a significant amount of dyes are lost as dyeing effluents, which finds its way into the environment. Out of several synthetic dyes used for dyeing of the fibre, more than 50% dye loss is associated with the reactive azo dyes because of its poor fixation efficiency (McMullan *et al*. 2001, Manu and Chaudhari 2002). Azo dyes are the most extensively used dye types and constitute about 60-70% of the total dyes produced (Øllgaard *et al*. 1999, Jonstrup *et al*. 2011). These are xenobiotic compounds characterized by the presence of one or more azo group (–N = N–). Different physico-chemical, biological, advanced oxidation processes and usually a combination of these processes are employed to treat these wastewaters to meet the regulatory standards (Banat *et al*. 1996). The traditional aerobic biological processes do not effectively decrease the color of the textile wastewater (Gnanapragasam *et al*. 2011) and also generates large quantity of active biological sludge which needs further treatment before being discharged to the environment. The anaerobic biological processes can be considered as an energy efficient technology as less energy is required for its operation, and biogas (energy yielding) is produced as a byproduct (Isik and Sponza 2008, Sandhya *et al*. 2008).

However, the azo dye reduction under anaerobic conditions leads to the formation of various types of aromatic amines, which possess the potential toxicity and carcinogenicity. USEPA (2009) provides the evidence of different types of toxicity due to the monocyclic aromatic amines on the different test models, where 96-hour LC_{50} for the fish was reported in the range from 16.4 to 49.5 mg/L. The carcinogenic effects of these aromatic amines were well explained by numerous researchers (Skipper *et al*. 2010). The effectiveness of upflow anaerobic sludge blanket (UASB) reactor for treatment of textile wastewater containing azo dyes has been investigated (Isik and Sponza 2005, Somasiri *et al*. 2008, Verma *et al*. 2014) and the production of different types of aromatic amines in the effluents have been monitored. It has been reported that the generation of aromatic amines (AAs) in UASB reactors leads to decrease in COD reduction efficiency and increase of COD in the effluents. Along with the number of advantages associated with the UASB reactor, formation of AAs as the toxic by-products limits its applicability for the treatment of textile wastewaters. Therefore, introduction of an integrated process for effective treatment of textile wastewater may be proposed as one of the viable technology. Recently, some of the researchers investigated the application of organic polymers for the removal of different types of AAs (Akceylan *et al*. 2009, Yilmaz *et al*. 2010). Owing the fact for effective removal of AAs by the application of suitable polymer, this physico-chemical treatment can be employed in the form of post-treatment step for the treated effluents of UASB reactor. These polymers remove the AAs with the help of chemi-sorption onto the surface of the polymer flocs at a certain pH. On the other hand, advanced oxidation processes such as ultrasonication was also found to be effective to transform non-biodegradable pollutants into harmless substances (Lim *et al*. 2011a). It has been demonstrated by a few researchers (Öztekin 2011, Onat *et al*. 2010) that ultrasonication can potentially be used for the remediation of the carcinogenic AAs present in the wastewater. It has the potential for use in environmental remediation due to the formation of highly concentrated oxidizing species such as hydroxyl radicals ($HO^{\bullet}$), hydrogen radicals ($H^{\bullet}$), hydroperoxyl radicals ($HO_2^{\bullet}$) and H_2O_2, at localized high temperatures and pressures as illustrated in Eqs. (1) to (3).

$$H_2O \xrightarrow{\text{US}} OH^\bullet + H^\bullet \tag{1}$$

$$H^\bullet + O_2 \xrightarrow{\text{US}} HO_2^\bullet \tag{2}$$

$$2\,OH^\bullet \xrightarrow{\text{US}} H_2O_2 \tag{3}$$

These short lived but highly reactive species can react with impurities within the cavitation bubbles or with the other materials present in water with close contact to the cavitation bubble to induce sonochemical degradation (Wang *et al.* 2008). The deep oxidation during ultrasonic irradiation effectively transforms these aromatic amines into the aliphatic compounds. The phenomenon of aromatic amines degradation could be explained on the basis of deep oxidation of aromatic structure into the simpler aliphatic structure (Ma *et al.* 2007). Hydrolysis and pyrolysis are the main degradation mechanisms for the AAs degradation with ultrasound. During ultrasonication, the generated highly reactive free radicals attack AAs to form the hydroxyl amines followed by subsequent oxidation to aromatic nitroso, nitro compounds and finally to simpler organic acids such as acetic acid and formic acid (Song *et al.* 2007). However, US does not always produce total degradation predominantly in the case of hydrophilic compounds such as azo dyes.

Studies pertaining to the elimination of aromatic amines using chemical coagulation as well as ultrasonication are very terse. To the best of our knowledge, no such study has been observed in the literature related to the removal of aromatic amines generated from anaerobic textile wastewater treatment using synthetic coagulants. In the present study, an effort has been made to assess the suitability of chemical coagulation and the ultrasonication process as a post treatment option for UASB reactor treating synthetic textile wastewater containing different types of textile dyes including azo dyes.

The study was performed to assess the effect of coagulant dosage for chemical coagulation employing a composite coagulant as magnesium chloride (MC) aided with aluminium chloro-hydrate (ACH) in an equal ratio (MC+ACH), and the effect of sonication time and sonication power for ultrasonication. The effectiveness of the selected composite coagulant for treatment of synthetic textile wastewater was previously established by the same authors (Verma *et al.* 2012). Color removal and COD reduction were also monitored along with the AAs reduction in both the processes. On account of the chemical cost and to maintain the simplicity and wide applicability of the process, no pH corrections were applied before coagulation and sonication. All the experiments were performed at the original pH of UASB reactor effluents.

2. Materials and methods

2.1 Textile wastewater

The synthetic textile wastewater was prepared by mixing three commercial dyes in equal proportions namely, Reactive Black 5 (RB5) (azo), Congo Red (CR) (diazo) and Disperse Blue 3 (DB3) (anthraquinone) in tap water, making a total dye concentration of 200 mg/L, along with the various chemical additives such as starch, acetic acid, sucrose, sodium carbonate, sodium

hydroxide, sulphuric acid, detergent, and sodium chloride, which are commonly found in the effluents of textile industries (Verma *et al.* 2012). The characteristic wavelength of simulated dye wastewater was determined by running a scan of the dye solution on a UV-VIS spectrophotometer and the maximum absorbance wavelengths (λ_{max}) for RB5, CR and DB3 were found as 591, 502 and 638 nm respectively. The color content of the wastewater containing mixture of dyes was determined by taking the sum of the absorbencies measured at 591, 502 and 638 nm (Wang *et al.* 2007).

Major characteristics of synthetic textile wastewater: COD = 1980 ± 30 mg/L, pH = 10.5 ± 0.2, Abs (mixture) = Abs (591) + Abs (502) + Abs (638) = 2.3992.

2.2 Description and operation of UASB reactors

The UASB reactor made of Plexiglas having an effective volume of 4.62 L, with the dimension of 80 mm × 75 mm × 770 mm was used for the treatment of synthetic textile wastewater with the above mentioned composition. The performance of the reactor was monitored regularly by measuring a number of parameters such as percentage decolorization, COD reduction, bicarbonate alkalinity (B- alkalinity) and volatile fatty acid (VFA). After achieving steady-state, the production of TAAs due to reductive cleavage of azo bond present in the textile dyes was also monitored along with the above described parameters. Steady state was considered, when almost steady readings of percentage decolorization, COD reduction, B-alkalinity and VFA were appeared. At the steady state, 79% COD reduction, 84% decolorization was observed with UASB reactor operating at a hydraulic retention time (HRT) of 20 hrs, initial COD of 2000 mg/L with an organic loading rate (OLR) of 2.4 kg COD m^3/d.

Major characteristics of UASB effluents at steady state were: COD = 400 ± 20 mg/L, pH = 7.4 ± 0.2, Abs (mixture) = Abs (591) + Abs (502) + Abs (638) = 0.3925 to 0.4067, TAAs = 6.92 ± 0.5 mg/L.

2.3 Chemicals

Extra pure magnesium chloride (MC) and industrial grade (purity 30% w/w) aluminium chlorohydrate (ACH) were used as coagulants. 1.0 M H_2SO_4 and NaOH were used to adjust the desired pH. The other chemical additives used in the preparation of the synthetic wastewater were of analytical grade. The dyes were procured from Sigma chemicals, Germany.

2.4 Coagulation/flocculation test procedures

The optimum coagulant dosage required for efficient color, COD and TAAs reduction was determined by jar test method. 1 L beakers, containing 500 mL of wastewater were used for the coagulation experiments. The composite coagulant was added and mixed for 3 min under rapid mixing condition at 80 rpm. The solution was then mixed at slow flocculation at 30 rpm for 15 min and allowed to settle down for 20 mins. The supernatant from the beaker was taken for analysis.

2.5 Ultrasonic reactor operation and analyses

Textile wastewater with a volume of 200 mL was used at a time in the reaction vessel (Fig. 1) attached to the low frequency power ultrasonic reactor (Hielscher Ultrasound Technology, 300 W,
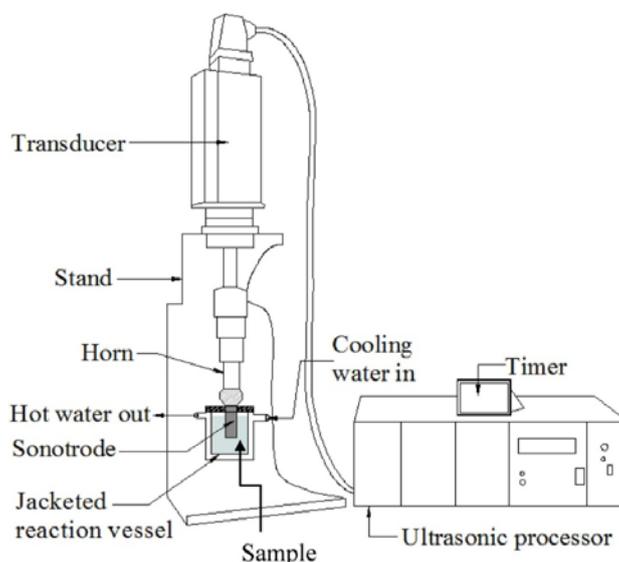
Fig. 1 Schematic diagram of lab scale ultrasonic reactor

20 kHz). The reaction vessel was equipped with a water cooling jacket to maintain a constant temperature throughout the sonication. After sonication, the sample was withdrawn, filtered with Whatman 42 filter paper (pore size = 2.5 μm). The pH of the filtrate was then adjusted to about neutral for measuring its absorbance. Subsequently, the color of the samples was determined by absorbance measurement using UV-vis spectrophotometer (Perkin-Elmeyer, Lambda 25) at the maximum absorbance wavelength (λ_{max}). The COD measurement was performed according to Standard Methods (APHA 1998), employing open reflux titrimetric method. All the experiments were performed at room temperature (26 ± 2°C).

The percentage decolorization efficiency was obtained by the Eq. (4)

$$\text{Decolorization efficiency (\%)} = \left[(A_i - A_t) \div A_t \right] \times 100 \tag{4}$$

where A_i is the initial absorbencies of UASB effluents and A_t the absorbencies after post-treatment of UASB effluents.

2.6 Monitoring of aromatic amines

Total aromatic amines (TAAs) were measured calorimetrically as per the method suggested by Oren *et al.* (1991). Analysis of aromatic amines was also performed by High Performance Liquid Chromatography (HPLC). For the HPLC analysis of aromatic amines, an aliquot of respective wastewater were centrifuged at 4000 rpm for 15 mins. The supernatants were transferred into a petri-dish which subsequently kept into the freeze dryer (Christ, ALPHA 1-2 LD plus) for the evaporation to its dryness. The residues were dissolved in methanol. Samples were filtered through a 0.22 μm nylon filter paper. Researchers investigated that RB5 and CR produce sulphanilic acid and benzidine like compounds, respectively after their reductive cleavage under the anaerobic environment (Isik and Sponza 2003, Lim *et al.* 2011b). HPLC was used to determine the presence

of these aromatic compounds in the samples. The samples were eluted isocratically by using a C18 column. The mobile phase used was a mixture of filtered methanol (HPLC grade) and Millipore water in 7:3 (v/v) ratio with a flow of 0.7 mL/mins. HPLC grade sulphanilic acid and benzidine served as a reference to obtain the information about the appearance of respective peaks.

3. Results and discussion

3.1 Determination of optimum coagulant dosage for chemical coagulation

The optimum dosage of coagulant for the treatment of UASB reactor effluents was determined by varying the coagulant dosage and maintaining its original pH. It has already a known fact that pH greatly affects the coagulation performance. However, in the present study marginal variation (within 2 to 3%) in the treatment efficiency was observed with a variation of pH of the UASB effluent. The optimum pH of the composite coagulant (MC + ACH) was found to be 12 (Verma *et al*. 2013). However, no significant difference in the treatment efficiencies was observed in the actual pH and optimum pH conditions for the present study (data not shown). Hence, the experiments were conducted in the actual pH conditions of the UASB effluent without any pH modification. Treatment efficiency with all the three selected parameters as a function of coagulant dosage is shown in Fig. 2. It was observed that color, COD and TAAs removal efficiency continuously increases with an increase in the coagulant dosage. At a (MC + ACH) dosage of 1800 mg/L, removal of color, COD and TAAs were found to be 85%, 52% and 31% respectively. The trend appeared in Fig. 2 depicts that the selected composite coagulant is more efficient for removing the color and COD as compared to the AAs present in the effluent. The observation may be linked with the fact that the colloidal nature of impurities (residual dyes) is much more susceptible to get neutralized by the action of the cationic nature of coagulant.
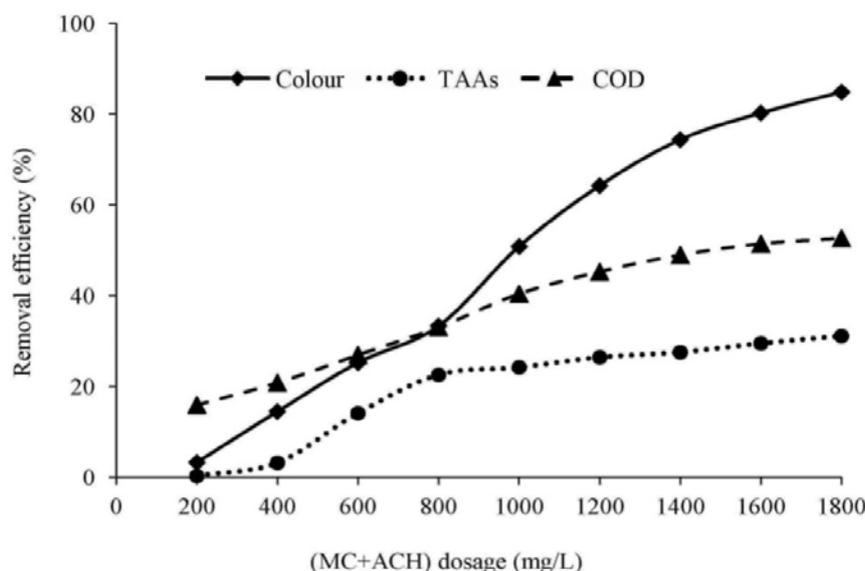

Fig. 2 Effect of coagulant dosage on color, COD and TAAs removal efficiency under the influent pH = 7.4

Further the coagulant removes the AAs by enmeshing them into the precipitated flocs (Akceylan *et al*. 2009). Insignificant AAs removal efficiency of applied coagulant may be related to the electrostatic repulsion between protonated AAs and the positively charged adsorption sites of coagulant. However, the diminutive increase in the removal efficiency with an increase in the coagulant dosage may be due to the structure of precipitated flocs, which might have been gaining the more rigid and appropriate structure with increased dosage, assisting the sorption of amines onto to the established floc matix (Akceylan *et al*. 2009). It is also possible that flocs formed after coagulation with sufficient amount of coagulant, achieved a certain degree of conformational stability where AAs could effectively associate. From the experimental results, it can be inferred that a (MC + ACH) dosage of 800 mg/L was found sufficient at which 24% of TAAs was removed, as no appreciable TAAs removal was observed beyond this dosage (Fig. 2).

3.2 Effect of ultrasonic power

The effect of applied US power on the treatment efficiency of the UASB reactor effluent was investigated by varying the power from 50 to 250 W at a regular interval of 50 W, maintaining sonication time of 60 mins. The results were plotted in the Fig. 3.

The degradation efficiency was continuously increasing with the increase in ultrasound (US) power up to 200 W (Fig. 3). No appreciable increase in removal of color, COD and TAAs was observed beyond 200 W, which indicates that the 200 W US power was sufficient for the maximum mineralization and degradation of the targeted impurities present in the wastewater. Application of ultrasound power produces cavitation bubbles, and the production of these bubbles increases with increasing acoustic power. Beyond an optimum acoustic power, these bubbles act as a barrier to the successful transfer of acoustic energy to the entire liquid medium (Contamine *et al*. 1995, Vajnhandl and Le Marechal 2007), which starts stabilizing the reaction rate and
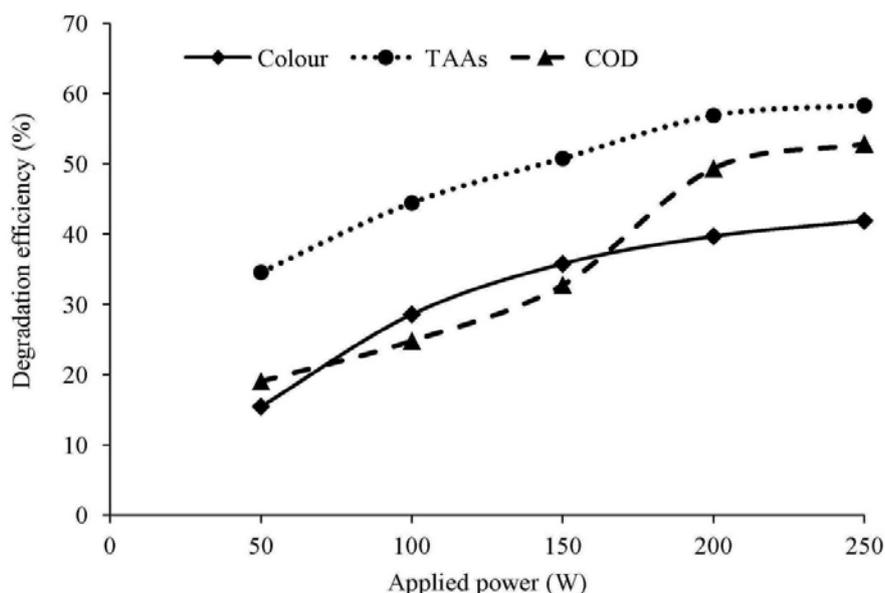

Fig. 3 Effect of power on the degradation efficiency under test conditions: sonication time = 60 mins

diminishes the degradation rate. The decrease in the degradation rate with increasing ultrasound power beyond an optimal value was also reported by numerous researchers (Su *et al*. 2012, Hao *et al*. 2014). Production of OH$^{\bullet}$ radicals, which are vital in oxidizing impurities, vastly depends on the applied energy to the reaction medium and eliminate the impurities effectively. Higher susceptibility of degradation of AAs towards ultrasonic power may be related to the effective transformation of AAs to aliphatic compounds under the deep oxidation during ultrasonic irradiation. The untransformed or partially transformed aromatic structures contribute in the COD and therefore decrease the COD reduction efficiency.

3.3 Effect of sonication time

The effect of sonication time on the degradation of targeted impurities present in UASB reactor effluents was investigated by varying the sonication time from 60 mins to 300 mins at an optimum ultrasonic power of 200 W.

A continuous increase in the decolorization efficiency to increase in the sonication time up to 240 mins was observed (Fig. 4). However, beyond the 240 mins sonication time, there was no appreciable increase in the decolorization efficiency. It is well established that ultrasonic wastewater treatment is a time dependent phenomenon. Higher sonication time produces higher number of cavitation bubbles, which cause interference for the transfer of acoustic energy in the whole liquid medium and start stabilizing the dye degradation. Therefore, sonication time of 240 mins was considered as optimum at which a maximum decolorization efficiency of 50% was achieved. TAAs and COD elimination also followed the same trend but the degradation rate of TAAs reduction was superior over the COD elimination rate. The observation may be attributed that the partially degraded aromatic amines contribute to increase of the COD value of the sonicated effluents.
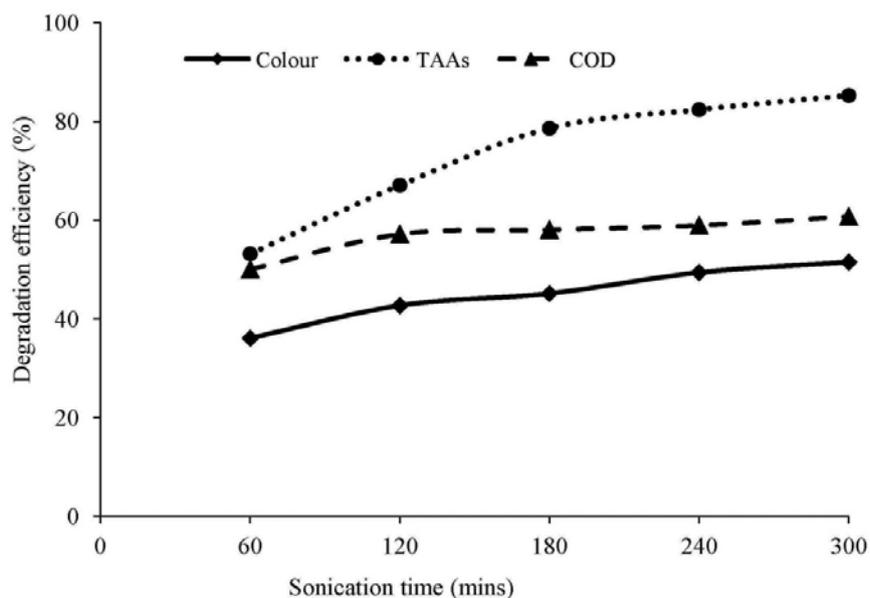

Fig. 4 Effect of sonication time on the degradation efficiency under applied US power = 200 W

Table 1 Comparative performance of both the processes

Process	Removal efficiency (%)		
	Color	COD	AAs
Chemical coagulation (Optimum dosage = 1800 mg/L)	85	52	31
Ultrasonication (Optimum power = 200 W; sonication time = 300 mins)	52	61	85

Comparing the results of both the processes of chemical coagulation and ultrasonication (Table 1), it can be said that color removal efficiency of chemical coagulation using MC + ACH was superior over the ultrasonication.

The lower degree of decolorization in ultrasonication process was observed due to the existence of very fine turbidity, that might be produced after partial solubilization and mineralization of the residual dye molecules mainly the undegraded DB3 dye present in the treated UASB effluents. DB3 is a recalcitrant textile dye and very difficult to be degraded even under extreme anaerobic conditions. However, partial removal of DB3 inside the UASB reactor is possibly due to its adsorption onto the biological sludge. Efficiency of ultrasonication for removal of TAAs was far superior over the coagulation process, while COD reduction efficiency was somewhat similar in both the processes. Analyzing the experimental results presented in Table 1, it can be said that ultrasonication effectively eliminates the targeted impurities and can be considered as one of the best alternatives to degrade the AAs efficiently. On the other hand, the enormous amount of chemical sludge production and limitations associated with its handling, chemical coagulation may not be the most attractive option for the efficient removal of AAs.

3.4 Scavenging effect of ultrasound towards aromatic amines

In order to observe the scavenging effect of ultrasonication towards the remediation of TAAs present in UASB reactor effluents, the assessment was carried out at constant ultrasound power of 200 W by varying the sonication time. A continuous decrease in the TAAs concentration was observed with increasing sonication time (Fig. 5).

A maximum of 85% TAAs removal was observed at a sonication time of 300 mins from an initial TAAs concentration of 6.92 mg/L. The phenomenon of aromatic amines degradation could be explained on the basis of deep oxidation of aromatic structure into the simpler aliphatic structure (Ma *et al*. 2007), where CO_2 and H_2O produce by the subsequent transformation of aromatic structures and their intermediates. The TAAs degradation rate was observed to attain steady state after a sonication time of 240 mins. High TAAs removal could be attributed to the higher mass transfer and higher surface area produced by the cavitation process (Entezari and Al-Hoseini 2007). Hydrolysis and pyrolysis are the main degradation mechanisms for TAAs associated with sonication. During sonication, the generated highly reactive free radicals attack TAAs to form the hydroxyl amines followed by subsequent oxidation to aromatic nitroso, nitro compounds and finally to simpler organic acids such as acetic acid and formic acid (Song *et al*. 2007). The attack by the free radicals at the carbon atom adjacent to the azo bond, may lead to production of phenyl derivative radicals (Öztekin 2011). Further reactions may also occur inside the cavitation bubbles, in the hypercritical water layer or in the bulk water as reported by Rehorek *et al*. (2004). The kinetics of TAAs degradation under the influence of US was also investigated (Fig. 6).
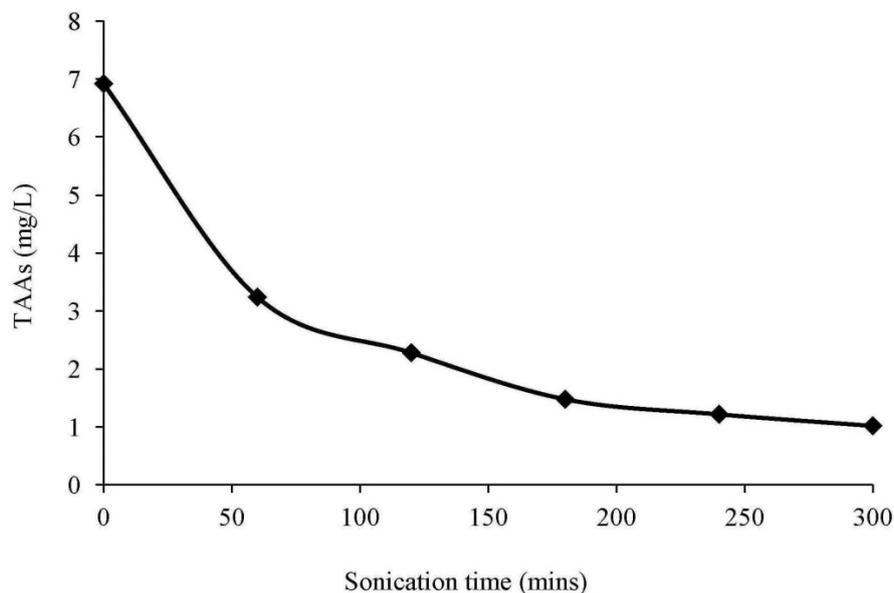
Fig. 5 Effect of sonication time on aromatic amines scavenging under test conditions: US power = 200 W, initial TAAs = 6.92 mg/L
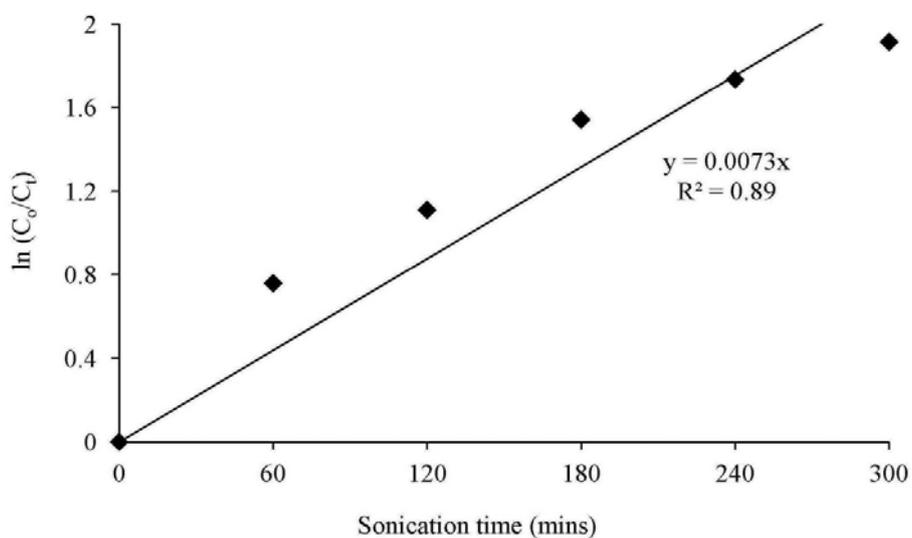

Fig. 6 Sonolytic TAAs removal kinetics of anaerobically pretreated textile wastewater effluent (C_o = Initial TAAs concentration, C_t= TAAs concentration at different sonication time)

It can be seen from the Fig. 6, that TAAs removal at a fixed ultrasound power of 200 W followed first order kinetics with a correlation coefficient (R^2) of 0.89 and a kinetic constant (k) of 0.0073 min^{-1}. The observed finding is in agreement with the results reported by Srivastava *et al*. (2014) for the degradation of different type of aromatic amines from the azo dye Acid Red 114.

3.5 Analysis of degradation products using HPLC

Numerous researchers (Isik and Sponza 2003, Lim *et al*. 2011a) reported the formation of sulphanilic acid and benzidine as the dead end aromatic amine products after the reductive cleavage of RB5 and CR. The chromatograms of sulphanilic acid and benzidine standard solutions were shown in Figs. 7(a) and 7(b). These standards with a concentration of 100 ppm were injected into the C18 column. Specific peaks were obtained for sulphanilic acid and benzidine standards at a retention time of 2.75 and 4.47 mins respectively. Chromatogram of UASB reactor effluent indicates the presence of sulphanilic acid and benzidine compounds (Fig. 7(c)), where similar peaks were also observed at a retention time of 2.76 and 4.47 mins. The analysis verifies the presence of suggested aromatic compounds which were produced during the reductive degradation of RB5 and CR dye inside the UASB reactor. However, the observed smaller peaks as compared to the sulphanilic acid and benzidine standards may imply the reduced concentration of these compounds in UASB reactor effluent.

A peak observed at 2.69 mins of retention time in UASB treated effluents may be due to the other possible intermediate formed during anaerobic process and its subsequent auto-oxidation
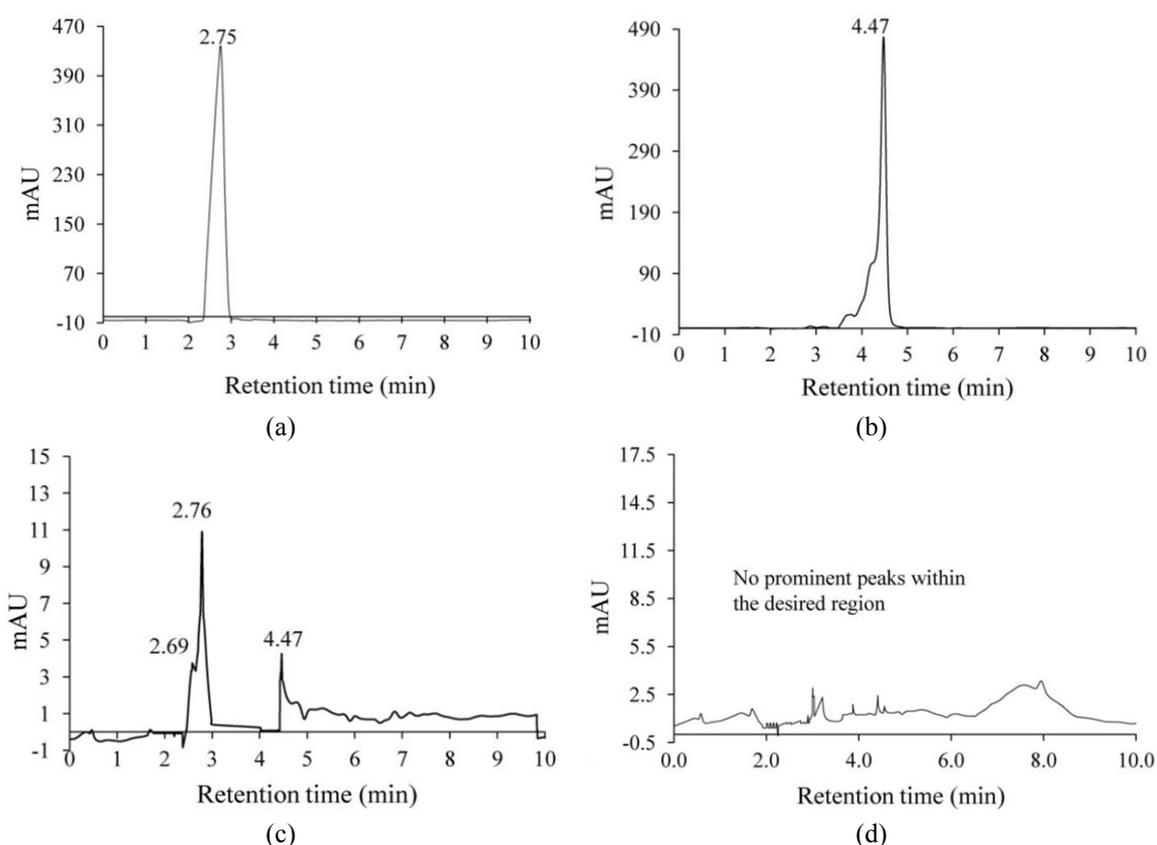
Fig. 7 Chromatogram showing the presence of aromatic amines in: (a) sulphanilic standard; (b) benzidine standard; (c) UASB reactor effluent; and (d) ultrasonically treated UASB reactor effluent

under the ambient environment, which cannot be degraded further (Fig. 7(c)). However, no prominent peaks were observed in the desired regions (Fig. 7(d)) for the ultrasonically treated UASB effluent, while a bit prominent peak can be seen beyond the desired regions. The observed peak indicates that the metabolites might be transformed to some other products, such as oligomers and polymers with low solubility (Field *et al*. 1995), due to their auto-oxidation under the oxidizing environment produced by the sonication.

4. Conclusions

The present study demonstrates the comparative efficacy of chemical coagulation and ultrasonication processes for degradation of residual impurities present in the UASB reactor effluents treating synthetic textile wastewater containing different types of textile dyes including azo dyes. The treatment efficiency of these two processes were assessed majorly based on the AAs removal capability, however, color and COD removal were also investigated for both the processes. Chemical coagulation produced an appreciable effect for decolorization producing a virtually colorless effluent (decolorization efficiency = 85%) while AAs removal efficiency was not significant (31%). On the other hand, excellent AAs degradation efficiency (85%) and considerable color removal efficiency (52%) was produced by ultrasonication process at a US power and sonication time of 200 W and 5 hrs, respectively. HPLC analysis depicted the presence of sulphanilic acid and benzidine as aromatic amines, which are the precursors of the utilized textile dyes. It can also be concluded that the ultrasonication effectively mineralizes AAs produced due to anaerobic treatment of azo dyes. The promising scavenging effect of sonolysis towards AAs may encourage the technology as one of the alternatives for the post treatment of anaerobically pre-treated textile wastewater.

Acknowledgments

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WL

Abbreviations

AAs	aromatic amines
abs	absorbance
ACH	aluminium chlorohydrate
BOD	biochemical oxygen demand
COD	chemical oxygen demand
HPLC	high performance liquid chromatography
HRT	hydraulic retention time
mAU	mili absorbance unit
MC	magnesium chloride
nm	nanometer
OLR	organic loading rate
TAAs	total Aromatic amines
UASB	upflow anaerobic sludge blanket
US	ultrasound
VFA	volatile fatty acid