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Review

Ultrasound in textile dyeing and the decolouration/mineralization of textile dyes

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Abstract

In recent decades ultrasound has established an important place in different industrial processes such as the medical field, and has started to revolutionize environmental protection. The idea of using ultrasound in textile wet processes is not a new one. On the contrary there are many reports from the 1950s and 1960s describing the beneficial effects of ultrasound in textile wet processes.

The aim of this paper is to review some fundamentals of ultrasound, its broad application and gather some new research and studies regarding ultrasound application in textile wet processes, with the emphasis on textile dyeing and the decolouration/mineralization of textile wastewaters.

Keywords: Ultrasound; Textile processes; Dyeing; Textile wastewater; Textile dyes; Decolouration; Degradation

1. Fundamentals of ultrasound

The chemical and biological effects of ultrasound were first reported by Loomis as early as 1927 [1]. Ultrasound spans the frequencies of roughly 18 kHz–10 MHz—beyond human hearing. In practice, three ranges of frequencies are reported for three distinct uses of ultrasound: low frequency or conventional power ultrasound (20–100 kHz), medium frequency ultrasound (300–1000 kHz) and diagnostic or high frequency ultrasound (2–10 MHz) [2,3].

Much like electromagnetic waves, ultrasonic waves can be focused, reflected and refracted; however unlike electromagnetic waves, they require a medium with elastic properties for propagation. Acoustic energy is a mechanical energy and it is not absorbed by molecules. When ultrasound passes through a liquid it induces vibrational motions of the intermolecular bonds, and energy is thus transferred through the medium in the propagational direction [2].

Ultrasound produces its chemical effects through several different physical mechanisms and the most important nonlinear acoustic process for sonochemistry is cavitation. Cavitation is the formation of gas-filled microbubbles or cavities in a liquid, their growth and, under proper conditions, implosive collapse [1]. The dynamics of cavity growth and collapse depend on the local environment and these parameters are discussed later.

Ultrasound waves consist of expansion (rarefaction) and compression cycles. Compression cycles exert a positive pressure on the liquid and push molecules together, while expansion cycles exert a negative pressure and pull molecules apart. Cavities can be generated during the expansion of a sound wave cycle with sufficient intensity, that the distance between the molecules exceeds the critical molecular distance necessary

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to hold the liquid together (for water molecules the critical molecular distance R is 10^{-8} m). As a consequence ''voids'' are created in the liquid. The intensity of the sound wave needed to induce cavitation depends on the type and purity of the liquid. Pure liquids have very great tensile strength, so available ultrasonic generators cannot produce significant negative pressures to create cavities. Fortunately, the liquids are impure and usually contain numerous small solid particles, pre-existing dissolved gases or, more especially the trapped gas–vapour nuclei, and the tensile strength of the liquid is reduced as a result. These solid particles and gas bubbles represent weak points in the liquid, the place where nucleation of the bubbles occurs [1,4–11].

A bubble in irradiated liquid continually absorbs energy from alternating compression and the expansion cycles of the sound wave. This causes the bubbles to grow in expansion cycles and contract in compression cycles. Two forms of cavitation are well known: stable and transient. Transient cavitation is usually produced with a high-intensity acoustic field. A transient cavity has a lifetime of one, or at most, a few acoustic cycles. In the meantime a bubble grows very rapidly to double its initial size and, finally, collapses violently in less than a microsecond. On the contrary at lower acoustic intensities, the size of the bubble oscillates in phases with the expansion and compression cycles. The bubble grows slowly over many acoustic cycles. This classification of cavitation is not strict, however, stable cavitation can lead to transient cavitation or a transient cavity can produce very small bubbles that undergo stable cavitation [1,4–6,8,10,11]. The critical sizes of the bubble depend on the liquid and the frequency of the sound. At 20 kHz the size of the bubble is roughly 170 μm and at 1 MHz it is 3.3 μm [7]. (Refer to the literature for details of the theoretical aspects of ultrasound and cavitation phenomenon [1,4–8, 10,11].)

Parameters which affect cavitation and bubble collapse (Table 1) are:

- *Properties of the solvent*: Cavities are more readily formed when using a solvent with high vapour pressure, low viscosity and low surface tension. But at high vapour pressure more vapour enters the cavitation bubble during its formation and the bubble collapse is cushioned and less violent [2,9,10].
- *Properties of gases*: Soluble gases should result in the formation of a larger number of cavitation nuclei, but the greater the solubility of the gas is the more gas molecules should penetrate the cavity. Therefore, a less violent and intense shock wave is created on bubble collapse. The polytropic ratio ($\gamma = c_p/c_v$) and the thermal conductivity of the gas have significant effect on the final temperature produced during cavity collapse. Higher temperatures and pressures are generated with monoatomic gases with larger ratios of specific heat (He, Ne, Ar) than diatomics (N_2, O_2), or polyatomic gases with lower heat capacity ratios (CO_2). The gas with the higher thermal conductivity reduces the temperature achieved during the collapse [2,3,6,9,10].
- *External pressure*: With increasing external pressure, the vapour pressure of the liquid decreases and higher intensity is necessary to induce cavitation.
- *External temperature*: Higher external temperature reduces the intensity necessary to induce cavitation due to the increased vapour pressure of the liquid. At higher external temperatures more vapour diffuses into the cavity, and the cavity collapse is cushioned and less violent. Therefore, sonochemical reactions proceed more slowly as ambient temperatures increase. The temperature near the boiling point of the liquid increases the number of bubbles which can act as a sound barrier [2,3,6,10].
- *Frequency of the sound wave*: Lower frequency produces more violent cavitation and, as a consequence, higher localized temperatures and pressures. At very high frequency, the expansion part of the sound wave is too short to permit molecules to be pulled apart sufficiently to generate a bubble. Weak cavitation or no cavitation in megahertz range is observed. [2,3,6].

There is no simple relationship between the discussed parameters, but this knowledge is crucial in designing

Table 1
Range of parameters that make cavitation easier or implosion more violent

	Characteristics of			
	Reaction medium	Sound wave	Gas	Other parameters
Positive effect on cavitation	high vapour pressure low viscosity low surface tension	low frequency (power US) greater intensity	high solubility	high external temperature low external pressure
Positive effect on implosion	low vapour pressure	low frequency (kHz region)	low solubility larger ratio of specific heat low thermal conductivity monoatomic gases	low external temperature high external pressure

experimental conditions so that the sonochemical effects are maximized.

1.1. Background of sonochemical reactions

The implosion of cavities creates an unusual environment for chemical reactions. The vapour and gases inside the cavity are extremely compressed during cavity collapse. Large increases in temperature and pressure are generated [8]. Furthermore, it is assumed [5] that cavitational collapse creates drastic local conditions: temperatures of about 5500 °C inside the bubble and 2100 °C in the liquid that surrounds the cavity, and pressure up to 100 MPa within the collapsing cavity [7]. Such conditions are limited to a very small region and the heat produced during cavitation is dissipated very quickly (heating and cooling rates greater than 10^9 K/s) [4]. As a result, the surrounding liquid remains at the ambient temperature. Organic compounds are highly degraded in such an environment and inorganic compounds can be oxidized or reduced. Water irradiation using ultrasound causes decomposition of the water molecules into extremely reactive radicals $HO^{\bullet}$ and $H^{\bullet}$. During the cooling phase these decomposed products can recombine and form hydrogen peroxide and molecular hydrogen [3,6,8,9].

There are different theories about sonochemical events but the origin of each theory is acoustic cavitation. A 'hot-spot' model is generally accepted, where each microbubble acts as a small microreactor which, during the collapse, produces different reactive species and heat. Three regions are postulated for the occurrence of chemical reactions: a hot gaseous nucleus, an interface between the bubble and the bulk liquid, and the bulk media. Free radicals or/and excited states are formed from water dissociation, vapours and gases or various substrates during bubble collapse, where high temperatures and pressures provide activation energy for homolytic bond breakage. The generated radicals either react with each other to form new molecules and radicals, or diffuse into bulk liquid to serve as oxidants. Combustion and free-radical reactions occur in the liquid shell surrounding the hot bubble. This area was estimated to have extended ~200 nm from the bubble's surface and had a lifetime of <2 μs [9,12].

It is believed that this region is of low polarity and thus allowing hydrophobic solutes to accumulate readily [3,9].

The major reaction site for hydrophilic compounds is the bulk media where they might be effectively destroyed by oxidative degradation, provided that sufficient quantities of hydroxyl radicals are ejected into the solution during cavity collapse. Maximum radical transfer occurs when the collapse of bubbles is "transient". In the bulk media intense shock waves and enormous shear forces are generated on the bubbles collapse.

Sonochemistry mainly deals with reactions which involve a liquid component's so-called homogeneous reactions. Reactions involving solid/liquid interfaces—heterogeneous reactions are also very important. There are two types of reactions involving solids and liquids; one in which the solid is a reagent and another in which it is a catalyst. In heterogeneous systems, cavitational collapse has two forms of influence. Shock waves produced on cavity implosion cause direct erosion on the solid's surface itself. Contrary, cavitational collapse close to a solid surface is markedly asymmetrical which generates a jet of liquid directed at the surface with a speed in the order of 110 m/s. This represents the well-known cleaning action of ultrasound. The microjets phenomenon can also be used to produce very fine emulsions from immiscible liquids. A good example is the hydrolysis of commercially important oils, fats and waxes in aqueous sodium hydroxide.

Cavitation and all the results of this phenomenon (release of temperature and pressure, intense shear forces, shock waves, microjets) have important beneficial effects on chemical reactions:

- acceleration of the reaction (also radical reactions),
- promotion of the mass transfer,
- higher efficiency of the catalyst,
- generation of useful reactive species,
- possible switching of the reaction pathway,
- reduction of the reaction steps.

Ultrasound-assisted reactions are performed under less forceful conditions, and crude or technical reagents can also be used. Old synthetic processes which have fallen into disuse due to low efficiency or expense can be revitalized by ultrasound [6,10,11].

Some other reported applications of ultrasound in the chemical and allied industries are presented in Table 2 [1,10,13].

2. Ultrasound in textile dyeing

Ultrasound allows for process acceleration and attainment of the same or better results than existing techniques under less extreme conditions, i.e., lower temperature and lower chemical concentrations. Textile wet processes assisted by ultrasound are of high interest for the textile industry for this reason. A review of earlier studies using ultrasound in textile wet processes was compiled by Thakore et al. [14]. There are also some reports on the application of ultrasound relating to the preparation of auxiliary baths for processes such as the preparation of sizes, emulsions, dye dispersions and thickeners for print paste. In spite of encouraging results from laboratory-scale studies, the ultrasound-assisted

Table 2
Widespread applications of ultrasound

Organic chemistry	Inorganic chemistry	Food technology	Ecology	Pharmaceutical industry	Medicine	Other industry
-modification of polymers	-preparation of activated metals by reduction of metal salts	-emulsification	-degradation of polymers	-biological cell disintegration (extraction of active antigens for making vaccines and in the study of lipids, enzymes and viruses)	-ultrasonic imaging	-ultrasonic plastic and metal welding
-synthesis of polymers	-generation of activated metals	-mixing	-sonolysis of organic pollutants in water	-ultrasonic airborne drying (temperature-sensitive powders-pharmaceuticals)	-ultrasound NMR	-metal cutting
-preparation of organometallic compounds from main group or transition metals	-precipitation of metal oxide catalysts (Cr, Mn, Co)	-blending			-diagnostic ultrasound	-machining of hard, brittle materials
	-impregnation of metals or metal halides on supports	-extraction			-enzyme activation	-ultrasonic soldering
	-preparation of activated metal solutions (e.g. colloidal alkali metal solutions, suspension of Mg or Hg)	-crystallization			-therapeutic ultrasound-induction of thermolysis in tissues (cancer treatment)	-ultrasonic cleaning (the primary use in electronic and optical industry)
	-crystallization and precipitation of metals, alloys, zeolithes and other solids	-foam destruction			-ultrasonic cleaning	-deburring
	-agglomeration of crystals	-degassing of liquids			-ultrasonic atomization-in inhalation therapy, air humidification	-erosion testing
		-particle/aerosol precipitation				-degassing of melts
		-oxidation processes				-spray pyrolysis to form thin films or fine particles
		-influencing enzyme activity				-treatment of solid surfaces
		-sterilization				-dispersion of solids
		-ultrasonic airborne drying (temperature-sensitive powders-foodstuffs)				-preparation of colloids
						-ultrasonic fuel atomization
						-ultrasonic electroless plating
						-wetting and impregnation
						-ultrasonic sieving, filtration and micromanipulation
						-ultrasonic-aided development in advanced lithography

wet textile processes have not been implemented on an industrial scale as yet.

Textile material is basically a (bi)porous viscoelastic material made of either natural or synthetic fibres. The acoustic characteristics of different textile materials under low-intensity and high-intensity ultrasound have been the subject of investigation by Datar and later by Moholkar [15–17]. Diffusion and convection in the inter-yarn and intra-yarn pores of the fabric are limiting mass transport mechanisms. The intensification and acceleration of mass transport, particularly in the intra-yarn pores, are the basis for the improvement of wet textile processes. Mass transport intensification using a conventional approach such as elevated temperatures, is not always feasible, due to undesired side-effects such as fabric damage.

Warmoeskerken and co-workers [18] studied the mass transport intensification in laundry processes regarding the presence of power ultrasound. The basic idea was that ultrasound enhances the mass transfer by reducing the stagnant cores in the yarns. Results from this study indicate that the use of an ultrasonic bath, frequency 33 kHz, increases the rinsing of sodium chloride by a factor of 6.

Furthermore, Moholkar and Warmoeskerken [19] explored the relationship between the efficiency of ultrasonic textile washing and the process parameters such as: the position of the textile in the ultrasound wave field, the gas content of the textile and the washing medium. Results indicate that acoustic cavitation and the related effects, such as the formation of microjets are the principle physical mechanisms behind the ultrasonic textile washing process. In their new study they developed a simple semi-empirical methodology for estimation of mass transfer enhancement [20].

Some laboratory experiments using the de-oiling of polyamide and de-sizing of cotton in an ultrasound field were done by Vouters et al. [21]. The main goal of this study was to develop a specific ultrasonic energy device which could be adapted onto the jigger. Obtained results show that ultrasound technology represents a promising technique for intensifying diffusion and washing by the effect of cavitation, as well as for improving the effectiveness of processes when compared to traditional treatments, in particular de-oiling treatments. Application of such processes at the industrial level needs further optimisation.

Ultrasound-assisted textile dyeing was first reported by Sokolov and Tumansky in 1941. Over all these years a lot of work has been done using high frequency and low frequency waves to study the effects on dye dispersion quality, change in solubility of water soluble dyes and dye uptake by textile materials using a broad spectrum of natural and synthetic fibres. Improvements observed in ultrasound-assisted dyeing processes are generally attributed to cavitation phenomena and, as a consequence, other mechanical effects are produced such as:

- dispersion (breaking up of aggregates with high relative molecular mass)
- degassing (expulsion of dissolved or entrapped air from fibre capillaries)
- diffusion (accelerating the rate of diffusion of dye inside the fibre)
- intense agitation of the liquid

The acceleration in dyeing rates observed by many workers might be the cumulative effects of the above.

Dye molecules have a tendency to form aggregates in the solution and this tendency increases with the increasing relative molecular mass of the dye molecule, but the higher temperatures cause disaggregation. It is well known that ultrasonic energy causes decomposition of the dye aggregates in a solution, thereby keeping it in a monomolecular state. Cavitation and its physico-chemical consequences enhance the dyeing rate and economize on energy and time consumption. Changes in the particle size of the disperse dye C.I. Disperse Red 60 in a low frequency ultrasound field (26 kHz), and the effect of particle size on the exhaustion rate were investigated by Lee and Kim [22]. The volume (in percentage) of particle sizes in the range of 1–2 μm increased from 63 to 80%, those in the range of 4–10 μm from 10 to 16%, whereas particle sizes in the range of 65–72 μm decreased from 14 to approximately 0% during 1 h of ultrasound irradiation. The volume of small particles increased, whereas those of large particles decreased relatively. The results of this investigation confirm that ultrasound reduces the particle size of a disperse dye and, due to this fact, enhances the dye fixation.

A study by Thakore et al. [23] deals with the diffusion and permeability of C.I. Direct Red 81 through a cellophane film using a low frequency ultrasound of 20 kHz. The results obtained in the study show substantial increase in both diffusion and permeability coefficient.

Shukla and Mathur [24] studied the dyeing process of silk using cationic, acid and metal-complex dyes at low temperatures, assisted by a low frequency ultrasound of 26 kHz and compared the results of dye uptake with those obtained by conventional processes. Their results show that silk dyeing in the presence of ultrasound increases the dye uptake for all classes of dyes at lower dyeing temperatures (45 °C and 50 °C) and a shorter dyeing time (15 min), as compared with conventional dyeing at 85 °C for 60 min (Table 3). Furthermore, there was no apparent fibre damage caused by cavitation.

A study by Saligram et al. [25] investigated the effect of ultrasound on the dyeing of polyester fibres with C.I. Disperse Orange 25 and C.I. Disperse Blue 79 dyes.

Table 3
Examples of ultrasound-assisted dyeing of different materials compared to conventional

Material	Pre-treatment	US equipment	Dyeing					
			Dye	Conventional	Results absorbance	Ultrasound	Results absorbance	Remarks
Silk filament yarn	degumming bleaching	ultrasonic bath 26 kHz/120 W	C.I. Basic Blue 9	85 °C/60 min 50 °C/30 min	∼0.028 ∼0.016	45 °C/15 min 50 °C/15 min	∼0.039 ∼0.048	-absorbance was measured in extracted dye solutions from 10 mg of the dyed material -higher absorbance value indicate greater dye uptake
			C.I. Basic Green 4	85 °C/60 min 50 °C/30 min	∼0.23 ∼0.175	45 °C/15 min 50 °C/15 min	∼0.38 ∼0.47	
			C.I. Acid Blue 45	85 °C/60 min 50 °C/30 min	∼0.038 ∼0.028	45 °C/15 min 50 °C/15 min	∼0.062 ∼0.078	
			C.I. Acid Red 106	85 °C/60 min 50 °C/30 min	∼0.18 ∼0.14	45 °C/15 min 50 °C/15 min	∼0.34 ∼0.38	
			C.I. Mordant Red 19	100 °C/60 min 50 °C/30 min	∼0.05 ∼0.022	45 °C/15 min 50 °C/15 min	∼0.075 ∼0.088	
Polybutylene terephthalate filament yarn	swelling addition of carrier	ultrasonic bath 26 kHz/120 W	C.I. Disperse Orange 25	100 °C/60 min 50 °C/30 min	0.341/0.362 0.108	50 °C/30 min 45 °C/30 min	0.29/0.330 0.319	-absorbance was measured in extracted dye solutions from 10 mg of the dyed material
			C.I. Disperse Blue 79	100 °C/60 min	0.152	50 °C/30 min	0.217	
Polyethylene terephthalate staple fibres			C.I. Disperse Orange 25	100 °C/60 min	0.103/0.110	50 °C/30 min	0.068/0.083	-results are refer to fibres swollen with benzyl alcohol
			C.I. Disperse Blue 79	100 °C/60 min	0.165	50 °C/30 min	0.143	
Cotton fibres	scouring bleaching	ultrasonic probe-frequency not reported	C.I. Reactive Red 120	80 °C/100 min	–	80 °C/100 min	–	-about 2% increased dye exhaustion under US for C.I. Reactive Red 120 and 6% for C.I. Reactive Black 5
			C.I. Reactive Black 5	40 °C/100 min		40 °C/100 min		

Material	Pre-treatment	US equipment	Dyeing					
			Dye	Conventional	Results fixation (%)	Ultrasound	Results fixation (%)	Remarks
Nylon-6	scouring bleaching	ultrasonic cleaner 38.5 kHz/500 W	C.I. Reactive Red 55	pH = 4	60.13	pH = 4	63.97	-fixation was determined after alkaline soaping
			C.I. Reactive Red 24	70 °C/60 min	49.67	350 W/60 min	55.09	
			C.I. Reactive Blue 19		76.90		94.74	
			C.I. Reactive Black 5		82.50		88.67	

Swollen and unswollen PBT and PET fibres were dyed with and without low frequency ultrasound under different conditions regarding time and temperature. In some cases dilatin was used as a carrier. Carriers are known to act as plasticising/swelling agents to open up the fibre structure. The results from this investigation show that ultrasound enhanced the diffusion of dye molecules into the fibres, although the levels of dyeing are not as high as in conventional commercial dyeing processes. The addition of a carrier enhanced the dye uptake. The effect of a carrier and ultrasound together was significantly larger than either individually. The preswelling process was found to improve dyeability. Similar investigation was performed by Ahmad and Lomas [26]. In a study of Lee et al. [27] the influence of ultrasound on the dyeing behaviour of PET fibres is investigated using C.I. Disperse Red 60 which has a highly crystalline structure and C.I. Disperse Blue 56 with a poor crystalline structure. Results from their previous study [22] indicate that ultrasound has a significant effect on the reduction in particle size of C.I. Disperse Red 60. Experimental observation from this study [27] confirms this fact for C.I. Reactive Red 60, but it is very interesting that there is no significant influence attributed to ultrasound on dye uptake and dyeing rate for C.I. Disperse Blue 56.

Öner et al. [28] studied the ultrasound-assisted dyeing of cellulosic fabrics with C.I. Reactive Red 120 and C.I. Reactive Black 5. The dyeings were carried out conventionally, and with the use of ultrasonic techniques, were compared in terms of percentage exhaustion, total amount of dye transferred to the washing bath after dyeing, fastness properties and colour values. Results obtained in this study indicate that ultrasound improved dye fixation and increased the percentage exhaustion for both reactive dyes, but had no effect on the fastness properties of the dyed materials. Improvements in dye uptake on cotton were observed by Mock et al. [29]. Cotton was dyed with the direct dyes Solophenyl Blue FGL 220 and Solophenyl Scarlet BNL 200. Both dyes needed a relatively large amount of salt for exhaustion. The important facts of their study were that dyeing with direct dyes at lower salt levels approaches the same final exhaustion as dyeing at higher salt level without ultrasound, ultrasound has the greatest effect on dyeing at low temperatures and, in addition, they found that it can reduce the amount of salt and energy required compared to a conventional process.

The ultrasound-assisted dyeing of nylon-6 fibres was first investigated by Shimizu and co-workers [30] and later by Kamel et al. [31,32]. It seems that nylon-6 fibre is very susceptible to low frequency ultrasound-assisted dyeing with various classes of dyes at different temperatures and under different reaction conditions, i.e., ultrasound power, pH of the medium and initial dye concentration. Dyeings with disperse, acid, acid mordant and reactive dyes in a low ultrasound field (27 kHz and 38.5 kHz) were investigated and, in all cases, increases in dyeing rate and decreases in activation energies were observed. Furthermore, Kamel established that dye uptake is enhanced in the dyeing diffusion phase. These experimental results confirm the observations of other authors that the enhancing effect is attributed to de-aggregation of the dye molecules, which leads to better dye diffusion and possible assistance for dye–fibre bond fixation.

There are also some reports regarding the use of power ultrasound in leather dyeing [33–36]. It was discovered that ultrasound-assisted dyeing increases the degree of dye penetration through the pores of the leather matrix, shortening the process time, facilitating low temperature dyeing and improving the fastness properties in comparison to conventional leather processing. It is evident from these studies that ultrasound is best applied in the initial stage of dyeing for a short period of time and is most effective in a dyeing system which has difficulty in achieving high dye exhaustion or penetration. A very important aspect also is that ultrasound seems more effective than mechanical stirring, and a combination of both can significantly enhance the dyeing process. A review of power ultrasound application in different stages of leather processing was performed by Sivakumar and Rao [34].

3. Textile dye remediation

The textile industry, as we know, consumes large volumes of clean and pure water in different wet processes and, therefore, produce enormous amounts of textile wastewater which is heavily charged with unconsumed dyes and other chemicals. Many textile dyes which are very diverse in chemical structure are very difficult to decolourize with conventional biological treatment. Unconsumed dyes in wastewaters impose serious aesthetic and environmental problems because of their colour and their high chemical oxygen demand. Moreover, direct discharge of such effluents can cause the formation of toxic aromatic amines under anaerobic conditions in waters, and contaminate the soil and groundwater. Accordingly, the management of dyehouse effluents requires an integrated approach to both problems; effluent treatment and water consumption, by developing suitable treatments that produce harmless effluents and recyclable water [37–40].

Ultrasonic irradiation shows promise and 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, and localized high temperatures and pressures. Sonochemical effects like pyrolytic and radical reactions have been observed

Table 4
Studies utilizing ultrasound in decolouration and mineralization of textile dyes

Textile dye	Treatment process	Experimental conditions	Goals of study	Observations/degradation efficiency/degradation products	Ref.
C.I. Reactive Black 5	sonolysis, ozonation, US/O_3	520 kHz piezoelectric transducer (1.63 W/cm^2), ozone 3.36 g/L, flow rate 50 L/h, air, $T = 20 \pm 0.5$ °C, 600 mL of 10, 20, 40, 50, 60 µM areated dye solutions, pH = 7, contact time at least 20 min	-decolouration and mineralization	-colour removal using US/O_3 twice as fast than with O_3 -US alone quite ineffective in decolouration -TOC removal for 20 µM dye solution in US/O_3, O_3, US was 76%, 50%, 2% after 1 h	[38]
Astrazon Red GTLN Maxilon Blue GRL Maxilon Blue 5G Astrazon Golden Yellow GL Astrazon Green M Yoracryl Brilliant Red Sandolan Yellow	sonolysis, electrolysis, sonoelectrolysis	510 kHz ultrasonic bath (1.1 W/cm^2) and 20 kHz probe system (20–100 W/cm^2), sealed electrolysis cell; Pt and C electrodes, electrolytes NaOCl, NaCl, KCl, KNO_3, Na_2SO_4	-function of electrolyte type, electrolyte concentration, current density, ultrasonic intensity, reaction temperature, type of electrodes	-deggasing at the electrode surfaces -disruption of the diffusion layer -improvement of mass transport of ions -cleaning and activation of the electrode surfaces -improvement of electrochemical process using high and low frequency ultrasound	[42,43]
Cuprophenyl Yellow RL	UV/H_2O_2/US	no data for US frequency, six mercury UV lamps-PL-S 11W TUV, 30% H_2O_2, 4.5 L of 0.1 g/L dye solution, contact time 1 h	-effect of different pH and H_2O_2 dosages on dye decolouration and degradation	-higher pH values facilitate decolouration -dosages of H_2O_2 lower than 0.1 mL/L accelerate decolouration, while no evidence effect was observed beyond 0.1 mL/L -TOC removal was greatly enhanced at dosages of H_2O_2 up to 1 mL/L at pH = 11	[44]
Acid Orange 7 (purified)	sonolysis, γ-radiolysis	640 kHz transducer type, O_2, 82 µM dye solution	-determination of intermediates and end products -prediction of reaction pathways	-hydroxybenzenesulfonic acid, 1,2-naphthaquinone were detected as intermediates -oxalate and formate ions were the most probable end products after 6 h	[45]

Acid Red 1 Acid Orange 8 Both purified	sonolysis, photocatalysis, sonophotocatalysis	20 kHz ultrasonic horn (37 W/L), TiO_2-surface area 35 m^2/g, 250 W lamps emitting at 315–400 nm with average emission intensities of 4.5×10^{-8} and 5.8×10^{-7} Einstein s^{-1} cm^{-2}, 0.1 g/L of TiO_2, $2–7 \times 10^{-5}$ M dye solutions, 2×10^{-5} M $FeCl_3$, air, $T = 35 \pm 1$ °C	-degradation and mineralization rates at different initial dyes concentrations and amount of photocatalyst -monitoring the evolution of H_2O_2 -effects of Fe(III) addition	-substrates followed pseudo first order kinetic -the greatest rate constant was achieved by sonophotocatalysis at different initial dye concentrations and amount of TiO_2 -with increasing dye concentration at constant amount of TiO_2 reaction rate decrease or stay constant in the case of US + TiO_2 treatment -US may induce the de-aggregation of the photocatalyst and increase its surface area -US accelerate mass transport between the solution phase and the photocatalyst surface -US increases the amount of radicals through cavitation phenomena	[46]
Acid Red B	sonolysis	50 kHz, 150 W cleaning bath, MnO_2-surface area 29.3 m^2/g, $T = 22$ °C, 100 mL of the dye solution with concentration 100 mg/L and pH = 3, 1 or 2 g/L MnO_2, preaerated for 20 min with O_2 or Ar with a flow rate of 100 mL/min, contact time for US 240 min	-effect of initial pH and anions (Cl^-, NO_3^-, SO_4^{2-}) on decolouration efficiency on MnO_2 -degradation of the dye on MnO_2 in the presence of US under O_2 or Ar atmosphere	-decolouration of the dye (100 mg/L) on MnO_2 (2 g/L) alone was highly pH depended and increased with decreasing pH -NO_3^-, SO_4^{2-} ions dramatically decreased adsorption process on MnO_2 especially at high concentrations of the dye -US enhanced decolouration of the dye on MnO_2 from 77.03% (MnO_2 alone) to 92.88% (US + MnO_2, O_2) and 98.93% (US + MnO_2, Ar) -US reduced the particle size of MnO_2 and consequently increase the active surface area -hydrogen peroxide formation rate was higher in the presence of Ar; $k_{Ar} = 1.21$ μM/min, $k_{O_2} = 0.66$ μM/min	[47,48]

(*continued on next page*)

Table 4 (*continued*)

Textile dye	Treatment process	Experimental conditions	Goals of study	Observations/degradation efficiency/degradation products	Ref.
C.I. Acid Orange 7	sonolysis + ozonation, sonolysis + UV irradiation, sonolysis + UV irradiation + ozonation, ozonation + UV irradiation, sonolysis, ozonation	520 kHz piezoelectric transducer, UV lamps-max emission at 253.7 nm, ozone, 1200 mL of 57 μM dye solution with pH = 5.5 aerated for 1 h, $T = 25 \pm 1$ °C, argon, oxygen, contact time 60 min	-effect of high frequency ultrasound and its combinations with O_3, UV light and both on dye degradation, TOC reduction and BOD_5 -optimize operation parameters such as ultrasonic power density, ozone flow, UV intensity, gas-flow rate	-the pseudo-first order absorbance decay coefficient was the greatest at a flow ratio of $Ar:O_2 = 1:0.5$ and power density of 0.073 W/mL -decolouration using only US was rather slow, three and half times faster with O_3 or UV and no significant improvement using US + UV + O_3 treatment -maximum mineralization of the dye was achieved in US + UV + O_3 treatment (around 40%) -performance of O_3-containing schemes was incomparably better (3.18 mg/L for all three combinations) than that of US or US + UV combination (0.69 mg/L) for inducing biodegradation	[49]
Acid Orange 5 Acid Orange 52 Direct Blue 71 Reactive Black 5 Reactive Orange 16 Reactive Orange 107	sonolysis	850 kHz, 60, 90, 120 W, 100 mL 100 μM dyes solutions, $T = 30$ °C, laccase	-dyes degradation and intermediates observation -toxicity test of treated dyes using respiratory inhibition test of Pseudomonas putida -effect of US on enzymatic deactivation	-increasing the power from 90 to 120 W increases the degradation rates for all dyes (the least for Direct Blue 71 and hydrolyzed Reactive Black 5) -radicals were rather formed at higher powers (14.9 μM/min at 120 W and 0.1 μM/min at 60 W) -after 12 h treatment Reactive Orange 16 showed the highest final respiratory inhibition (13%) of Pseudomonas putida -at low energy levels simultaneous application of US and laccase might be feasible	[50]
C.I. Reactive Red 141 C.I. Reactive Black 5 C.I. Basic Brown 4 C.I. Basic Blue 3	sonolysis	520 kHz plate type piezoelectric transducer, 0.126 W/mL, 300 mL 20 mg/L dyes solutions aerated for 1 h with pH = 5.5–6.5, contact time 4 h, Ar with flow rate of 3 mL/min, $T = 20 \pm 0.5$ °C	-decolouration of dyes solutions at optimal power density -toxicity test of irradiated dyes using luminescent bacteria Vibrio fischeri	-more than 80% decolouration of all dyes was achieved within 120 min, while for any reduction of absorbance in UV region longer contact time is needed (4 h) -5 and 15 min toxicity test of reactive dyes showed non-toxic character at 20 and 30 mg/L, while basic ones were toxic at both concentrations	[51]

Rhodamine B	sonolysis	ultrasonic horn 1: 22.5 kHz, 600 W, dissipating area of tip 1.1 cm^2, ultrasonic horn 2: 22.5 kHz, 240 W, dissipating area of tip 0.9, 1.5, 3.5, 4.9 cm^2, ultrasonic bath: 22.5 kHz, 120 W, dual frequency batch reactor: 25 and/or 40 kHz, 120 W each, 10–1500 mL 5–10 μg/mL dye solution, $T = 25 \pm 2$ °C, contact time 30 min	-achieved maximum dye degradation with optimum power density and power intensity using different ultrasonic equipments	-degradation not increase indefinitely with[52] increasing power parameters but there always exist optimum value -optimum operation parameters were not the same in used equipment

between the 20 kHz and 1 MHz frequency range. The highest efficiencies were reported above 200 kHz. In the low frequency range between 20 kHz and 100 kHz, the hydromechanical effects such as shear forces and jet-streams are predominated [41]. Although several studies report the beneficial use of ultrasonic irradiation for the decolouration of various textile dyes, the total mineralization of these complex compounds is difficult to obtain with ultrasound alone. For this reason the combination of ultrasound with other advanced oxidation processes is a more convenient approach in the remediation of such pollutants.

Adewuyi [9] has already gathered studies involving the use of sonochemical or photosonochemical processes to treat a variety of chemical contaminants such as aromatic compounds, chlorinated aliphatic hydrocarbons, explosives, herbicides and pesticides, organic dyes, organic and inorganic gaseous pollutants, mostly in aqueous media. In the textile industry these are very interesting and encouraging results in the decolouration and mineralization of the azo dyes Remazol Black B (investigated by Vinodgopal et al.) and Naphthol Blue Black (investigated by Stock et al.) after long exposure to high frequency ultrasound. It seems that the ultrasound-assisted decolouration and mineralization of textile dyes has become quite an interesting research area confirmed by several reports over the last few years. Some of them are presented in Table 4.

The term "mineralization" means that the final products of the degradation process are carbon dioxide, short-chain organic acid, oxalate, formate and inorganic ions like, sulphate and nitrate.

4. Conclusion

Textiles, and their end products, constitute the world's second largest industry, placed only below food products. At least 10% of the world's productive energies are devoted to this activity [53]. Current wet textile processes suffer from two major drawbacks: large process time and low energy efficiency. Despite over 100 years of process improvements, the preparation, dyeing, and finishing of textiles continues to utilize large volumes of pure, clean water.

Ultrasound, and its beneficial effects, offer the potential for shorter reaction cycles, cheaper reagents, and less extreme physical conditions, leading to less expensive and, perhaps, smaller plants [54,55]. It is believed that of all wet textile processes ultrasound-assisted dyeing is the most promising area. Ultrasound-assisted dyeing lowers the dyeing temperature and shortens the dyeing time, achieving the same or even better colour exhaustion in comparison to conventional dyeing for mostly all kinds of fibres with the exception of the low temperature dyeing of polyester fibres. Less dye and other auxiliaries are needed to obtain the required colour and less effluent is produced. The introduction of ultrasound in dyeing processes seems to be the most convenient. Firstly, when dyeing with direct dyes which require a large electrolyte addition to achieve exhaustion, secondly with disperse dyes, which exhaust only with a carrier or under high temperature, and finally with reactive dyes which require large amounts of electrolyte for fixation.

Recently, there has been a great deal of research into resolving environmental problems caused by textile dyeing and finishing processes. Various novel processes are being introduced and ultrasound is also being studied as an alternative solution for environmental problems. This process works on the principle of generating free radicals and their subsequent attack on the contaminant molecules with the aim of either, completely mineralizing the contaminants or converting it into less harmful or lower chain compounds which can then be treated biologically.

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