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Ultrasound aided $KMnO_4$-acid systems for bleaching linen fabric

A. Hebeish, S. Sharaf*, M.M. Abd El-Hady

National Research Centre, Textile Research Division, P.O. Box 12622, Dokki, Cairo, Egypt

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ABSTRACT

Investigations were undertaken to optimize bleaching of linen fabrics using four systems, namely, $KMnO_4$-oxalic acid, $KMnO_4$-citric acid, ultrasound assisted $KMnO_4$-oxalic acid and ultrasound assisted $KMnO_4$-citric acid .The bleaching process involved two distinct steps where linen fabric was treated under different conditions with aqueous solutions of $KMnO_4$ to yield MnO_2-containing fabrics then the latter in a subsequent step was subjected to acid treatment under a variety of conditions. Optimization studies concerning the KMnO4 treatment refer to the following conditions.

[KMnO4], 5 g/l at pH 4 and 90 °C for 20 min, whereas those of acid treatment were [oxalic acid], 10 g/l at 85 °C for 30 min. Similar conditions were found with citric acid except that its concentrations was 8 g/l. Introduction of ultrasound as an eco-friendly source of energy in the acid treatment step shortens the time from 30 min to 5 and 10 min in case of oxalic acid and citric acid respectively while decreasing the temperature from 85 °C to 60 °C for both acids.

1. Introduction

Loomstate linen fabric is produced through mechanical processing i.e., spinning and weaving of flax fibers. The latter essentially comprises three polymers, namely cellulose, lignin and matrix, polysaccharides such as pectic substances and hemicelluloses. Cellulose is present in the cell wall of the flax fiber along with a number of minor components such as wax, inorganic salts, nitrogenous substances, and coloring matters (Fakin, 2004; Sharma & Sumere, 1991). Some non-cellulosic components (impurities) exert negative effects on the dyeing and finishing processes of the linen fabric and must be removed by subjecting the loomstate linen fabric to scouring and bleaching process (Fakin, 2004; Hipp, Schirmer, & Holz, 1995) While alkaline, acidic and bioscouring have been reported for removal of the uncolored flax impurities (Fakin, 2004; Fakin, Golob, Kreze, & le Marechal, 2005). Oxidative bleaching with hydrogen peroxide is generally used for the decomposition of flax fiber natural pigments (Diller, Yang, & Yamamoto, 2001; Weck, 1990).

Efforts are being paid to establish new bleaching methods which are both environmentally friendly and economically viable (Sharma, 1989; Shenai, 1975). In this context bleaching method based on potassium permanganate is very promising (Fakin et al., 2005; Fakin, Golob, Kleinscheek, & Le Marechal, 2006). The permanganate is one of the most versatile oxidizing agents. According to previous reports (Shenai, 1975) some common oxidizing agents may be arranged in increasing order of their oxidizing ability as follows:

$$NaClO_3 < NaClO_2 < H_2O_2 < K_2Cr_2O_7 < KMnO_4 < NaClO$$

With the exception of sodium hypochlorite, the above order reveals that $KMnO_4$ is more powerful than most of the common oxidants used in textile bleaching.

The permanganate (MnO_{4-}) has the ability to oxidize inorganic or organic compounds under neutral, acidic and alkaline conditions in aqueous or non-aqueous media. The traditional formulation of permanganate oxidation under acidic conditions applies to a limited number of organic substrate, because only few organic compounds can reduce the intermediate MnO_2 to Mn^{2+}. Acidic conditions are more favorable than alkaline conditions for bleaching (Mortazavi, Ziaie, & Khayamian, 2008) as will be explained later.

Nowadays researchers are involved in developing innovative nontraditional techniques with a view to decrease processing time and energy consumption as well as to improve product quality. In this regard, ultrasound is of considerable interest for textile wet processing. The frequency of ultrasound is above the audiable range of a human being. Ultrasound is broadly divided into power ultrasound (18 khz–1 MHz) and diagnostic ultrasound (over 1 MHz) (Suslick, 1989a,b; Thakare et al., 1990). Wet processing of textiles is assisted by introducing ultrasonic energy into the processing bath causes significant acceleration in the physical and chemical processes mainly due to a phenomenon known as cavitation (Mason, 1999; Suslick, 1989a, 1989b).

* Corresponding author. Tel.: +20 233357807; fax: +20 233363261.
E-mail address: samarsami2004@yahoo.com (S. Sharaf).

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Cavitation is the growth and explosive collapse of microscopic bubbles. As sound waves pass through liquids, the sonic vibration generates a local pressure wave in addition to the ambient hydrostatic pressure, giving rise to cycles of compression and rarefaction. The microscopic bubbles form during rarefaction (negative pressure) cycles, and are crushed during the next compression cycle. The sudden explosive collapse of these bubbles can generate hot spots (Mason, 1999; Suslick, 1989a, 1989b)., .i.e., localized high temperature, high pressure shock waves and a severe shear force capable of breaking chemical bonds. Intense agitation, dispersion, emulsification, degassing, and micro-jetting as well as free radical generation and transient electrical effect occur (Mason, 1999; Suslick, 1989a, 1989b). The effect of cavitation is several hundred times greater in heterogeneous systems, e.g., all textile wet processes, than in homogeneous systems (Adewuyu, 2001; Fakin et al., 2005; Yachmenev, Blanchared, & Lambert, 1999). Rather to a conventional bleaching technique, an ultrasonic energy can therefore be adopted successfully and with this method much more whiteness Index (W.I) for the cellulosic materials can be obtained than the cold bleaching (Ilker Mistik & MÜge YÜkseloglu, 2005).

Our current work aims at developing $KMnO_4$- acid systems for bleaching scoured loom state linen fabric. Thus $KMno_4$-oxalic acid, $KMnO_4$-citric acid with and without being assisted by ultrasonic energy are studied under a variety of conditions Also studied is a comparison of bleaching using the developed method with conventional bleaching using H_2O_2 The effectiveness of bleaching using these four systems is evaluated through monitoring water absorbency (wettability), whiteness index, yellowness index and tensile strength of the fabrics before and after bleaching.

2. Experimental

2.1. Linen fabric

Grey 100% loomstate linen fabric (Plain weave, 270 g/m^{2}38 yarns/in. in warp and 30 yarns/in. in weft) was supplied by Egyptian Co. For textile Industry/Dintex, Cairo, Egypt.

2.2. Chemicals

Potassium permanganate, oxalic acid, citric acid, sulfuric acid (98%), hydrogen peroxide (35%) and acetic acid (96%) were of laboratory grade chemicals. Sodium silicate and Egyptol were of commercial grade chemicals.

2.3. Ultrasound equipment

A mode l300 series NEY. ULTRA sonik, cleaner controller ultrasonic bench. top cleaner bath with a 6 L tank, was used. The experimental set up was composed of an electrical generator with a frequency of 26 kHz and a maximum power 300 W .The output power levels ranged from 60 to 300 W., and were supplied by transducers at the bottom of the industrial grade tank. Adjustable power burst and degassing period with heat and cleaning cycle timer were also used in the model-The internal dimensions of the tank were 270 mm × 200 mm × 150 mm.

2.4. Scouring of loomstate linen fabric

Linen fabric was scoured for 30 min at 95 °C in the presence of 4 g/l sodium hydroxide, 9 g/l sodium carbonate and wetting agent 3 ml/l. Scouring process was followed by washing for 15 min at 80 °C.

2.5. Conventional bleaching using hydrogen peroxide

Scoured linen fabrics were treated with an aqueous solution containing hydrogen peroxide (5 g/l of 45% hydrogen peroxide) and sodium silicate (1 g/l). The pH was adjusted to 10.5 using aqueous sodium hydroxide and the bleaching process was carried out using liquor ratio 1:20 at 95 °C for 120 min. At this end, the fabric was washed several times with boiling water as well as with cold water and then dried at ambient condition.

2.6. Ultrasonic bleaching using hydrogen peroxide

Scoured linen fabrics were treated with an aqueous solution containing hydrogen peroxide (5 g/l of 45% hydrogen peroxide) and sodium silicate (1 g/l). The pH was adjusted to 10.5 using aqueous sodium hydroxide and the bleaching process was carried out using ultrasonic water bath at 60 °C for 60 min. At this end, the fabric was washed several times with boiling water as well as with cold water and then dried at ambient condition.

2.7. Bleaching using $KMnO_4$-acid system

Bleaching using $KMnO_4$ was carried out under different conditions including $KMnO_4$ concentration as well as temperature and duration of the $KMnO_4$ treatment. The starting pH 4 of the treatment was brought about using sulphuric acid/acetic acid mixture at a ratio of 3:4. The treatment was conducted using a material to liquor ratio 1:30. The so treated fabric was washed with running water. It was then divided into two parts. The first part was treated with oxalic acid using different concentration (6–12 g/l) at different temperatures (30–85 °C) for 30 min .At this end, the fabric was rinsed in boiling water for 1 min and finally dried. Similarly the second part was treated with citric acid (6–12 g/l) at (30–85 °C) for 30 min then rinsed in boiling water for 1 min followed by drying at ambient condition.

2.8. Bleaching using permanganate-acid system assisted by ultrasound for ultrasound application

After being treated with $KMnO_4$ under the optimum conditions, acid treatment was conducted under ultrasonic water bath for different time of sonication (5–20 min) for both acids. At the end of treatment the fabrics was washed several time with water followed by drying at ambient condition.

2.9. Testing and analysis

- Tensile strength was determined by the strip method according at ASTM D1682-64.
- Fabric whiteness and yellowness index of linen fabrics were evaluated with Color-Eye 3100 spectrophotometer from SDL inter (Welch & Peters, 1997).
- Fabric absorbency (wettability) was measured by means of drop test AATCC test method 39-1980.
- The obtained results of the aforementioned analysis and test methods are the average of triplicate tests.

3. Result and discussion

3.1. Tentative mechanism for bleaching

When the scoured linen fabric was impregnated in the potassium permanganate solution, it turned to brownish dark or black color of MnO_2, depending on the concentration of the permanganate solution. Previous report (Abdel Hafiz, El-Rafie, Hassan, & Hebeish, 1995) from our laboratories revealed that the MnO_2

content increases substantially by increasing the concentration of $KMnO_4$.

Mn^{IV} produces free radical species through reduction of Mn^{IV} to either Mn^{III} or Mn^{II} which in turn abstract hydrogen atom from the cellulose and resulting in cellulose macroradicals as shown under.

$$Mn^{IV} + H_2O \rightarrow Mn^{II} + H^+ + HO^\bullet \quad (1)$$

$$Mn^{II} + HO^\bullet \rightarrow Mn^{II} + H^+ + HO^\bullet \quad (2)$$

$$\text{Cell-OH} + HO^\bullet \rightarrow \text{Cell-O}^\bullet + H_2O \quad (3)$$

$$\text{Cell-OH} + Mn^{IV} \rightarrow Mn^{III} + H^+ + \text{Cell-O}^\bullet \quad (4)$$

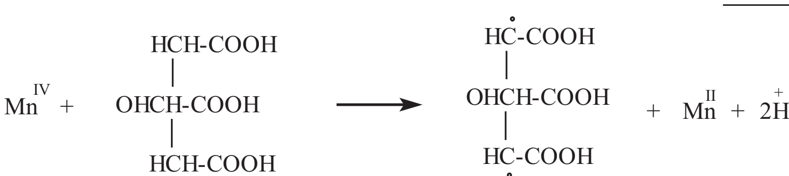
$$\text{Cell-OH} + Mn^{III} \rightarrow Mn^{II} + H^+ + \text{Cell-O}^\bullet \quad (5)$$

The hydroxyl free radicals (Eqs. (1) and (2)) can attack the coloring matter in the linen fabric and in so doing causes fabric bleaching. Similarly addition of oxygen to cellulose macro radicals leads ultimately to oxidized cellulose.

The formulations adopted in this work for bleaching linen fabric through oxidation of natural and other coloring materials relies on the $KMnO_4$-oxalic acid system and $KMnO_4$- citric acid system as well as these systems assisted by ultrasound energy.

$$2MnO_4^- + 5H_2O + 6H^+ \rightarrow 2Mn^{II} + 8H_2O + 5(O) \quad (6)$$

Eq. (6) indicates that the acidic condition of oxidation make 5 atoms of oxygen available for bleaching (Mortazavi et al., 2008). It is as well to note that the action of the acid on the deposited MnO_2 would create another radical species, for example, in case of citric acid under, the following primary free radicals are formed.



(7)

Whereas the primary free radicals formed In case of oxalic acid, the primary free radicals formed are represented by Eq. (8) as shown below.

$$Mn^{IV} + C_2O_4^{-2} \rightarrow CO^\bullet O^- + Mn^{III} + CO_2 \quad (8)$$

The free radicals formed according to Eqs. (7) and (8) acts in a way similar to those of Eqs. (1) and (2) with respect to coloring matter and linen cellulose.

When the ultrasound is employed to assist the $KMnO_4$-oxalic acid aqueous system or $KMnO_4$–citric acid aqueous system, additional free radicals and oxygen atoms are formed under the action of the ultrasonic energy as suggested by the following reaction scheme:

$$H_2O +))) \rightarrow OH^\bullet + H^\bullet(\text{Thermolysis}) \quad (9)$$

$$OH^\bullet + H^\bullet \rightarrow H_2O \quad (10)$$

$$OH^\bullet + H^\bullet \rightarrow H_2O_2 \quad (11)$$

$$2OH^\bullet \rightarrow H_2O + O \quad (12)$$

$$O_2 +))) \rightarrow O + O \quad (13)$$

$$O + H_2O \rightarrow OH^\bullet + OH^\bullet \quad (14)$$

$$O_2 + H^\bullet \rightarrow O_2H^\bullet \quad (15)$$

$$O_2H^\bullet + 2H^\bullet \rightarrow H_2O_2 + O_2 \quad (16)$$

It is obvious from the above reactions (suggested by Eqs. (1)–(16)) that the mechanism involved in bleaching linen fabric using the said $KMnO_4$–acid systems in single use or assisted by ultrasound is based on creation of various free radicals as well as oxygen atoms.

In the insight of the above mechanism the following investigations are performed in order to achieve the goal of current work. As already stated, we undertake the present work with a view to devise innovative techniques for bleaching scoured loomstate linen fabrics. The innovation is based on $KMnO_4$–acid systems with and without being assisted by ultrasonic energy.

3.2. Potassium permanganate ($KMnO_4$) concentration

The loomstate linen fabric in question was first treated at pH 4 with different $KMnO_4$ concentrations followed by washing as described in the experimental section. The so obtained fabric was treated further with either oxalic acid or citric acid in a subsequent step to expedite bleaching fabrics. Samples were then monitored for major technical properties encompassing whiteness index, yellowness index water absorbency and tensile strength. The results obtained are summarized in Table 1.

It is seen (Table 1) that with the $KMnO_4$–oxalic acid system whiteness index increase significantly by increasing the $KMnO_4$ concentration from 3 to 5 g/l. increasing the $KMnO_4$ concentration further to 7 g/l and above adversely affect the effectiveness of bleaching to the same extent. Similar trend is observed with $KMnO_4$–citric acid system except that the whiteness index continues to decrease after $KMnO_4$ concentration of 5 g/l that is, whiteness index exhibits a maximum value at 5 g/l $KMnO_4$ below or above this concentration, lower values of whiteness index are observed. Stated in other words, $KMnO_4$ concentration5 g/l constitutes the optimal for bleaching using $KMnO_4$–oxalic acid system or $KMnO_4$–citric acid system. At any event, however the former system is much more effective than the latter as far as whiteness index is concerned .It seems logical that at this particular concentration the most appropriate amount of MnO_2 is deposited onto the fabric. Under acidic conditions MnO_2 is reduced to Mn^{II} and, as a result, oxygen atoms are produced and become available for bleaching as shown by the reaction suggested by (Eq. (6)). The superiority of oxalic acid vis-à-vis citric acid is a manifestation of differences in acid strength and ability to generate free radicals as per (Eq. (7)) as well as to facilitate direct attack of Mn^{VI}, Mn^{III} and or Mn^{II} upon the coloring matter on fabric the decrement in whiteness index at higher $KMnO_4$ concentration (7 g/l and above) could be interpreted in terms of formation of higher amounts of deposited MnO_2 within the fabric structure. By virtue of the colloidal nature of MnO_2, the latter impedes diffusion of oxygen from aqueous phase to fabric phase thereby reducing the whiteness index of the fabric.

Results of Table 1 imply that the yellowness index generally decreases by increasing the $KMnO_4$ concentrations and attains its highest values at 9 g/l $KMnO_4$ which is the highest concentration used in this study. This is observed upon using $KMnO_4$–oxalic acid system or $KMnO_4$–citric acid system. The results also indicate that the absorbency (wettability) of the linen fabric enhances greatly to reach less than one second of a drop of water on the fabric to disappear (fully absorbed) provided that 5 g/l $KMnO_4$ or above was used irrespective of the acid used, the bleaching systems under investigation seems to purify the linen fabric from residual hydrophobic impurities thereby accentuating the water absorbency of the fabric.

Results of tensile strength (Table 1) make it evident that increasing the $KMnO_4$ concentration is accompanied by significant reduction in tensile strength. This is the case with both

Table 1
Effect of $KMnO_4$ concentration treatment on major technical properties of linen fabric.

$KMnO_4$ concentration (g/l)[a]	Oxalic acid[b]				Citric acid[b]			
	Absorbency (s)	Whiteness index	Yellowness index	Tensile strength (kg.f)	Absorbency (s)	Whiteness index	Yellowness index	Tensile strength (kg.f)
3	3	30.34	14.74	85	5	23.72	15.68	79
5	<1	36.88	10.90	75	<1	29.48	13.98	63
7	<1	34.43	13.18	68	<1	26.24	14.92	55
9	<1	34.22	8.07	66	<1	23.97	6.16	50
Blank*	5	-43	–	95	5	−43	–	95

[a] $KMnO_4$ bath: pH;4, Time; 20 min; Temperature; 90 °C, Material to liquor ratio 1:30.
[b] Acid bath—citric acid: 8 g/l; oxalic acid: 10 g/l; temperature: 85 °C; time: 30 min.
* Blank means scoured linen fabric.

bleaching systems though fabrics bleached as per $KMnO_4$–oxalic acid system retains more strength than those processed according to $KMnO_4$–citric acid system. This suggests that the latter system causes higher molecular degradation via oxidation of linen cellulose than does the $KMnO_4$–oxalic acid system. Oxidation of cellulose occurs as per equation (1–5) acid free radicals suggested by Eqs. (7) and (8) may contribute in this as well as in glucoside bond scission thereby shortening the cellulose chains and consequently decreasing the tensile strength. Depolymerization of linen cellulose to bring about shorter chain is unequivocally occurring under effect of acid via hydrolysis.

3.3. Duration of $KMnO_4$ treatment

The scoured loomstate linen fabric was treated with 5 g/l $KMnO_4$ solution at pH 4 using liquor ratio of 30 for different durations. The $KMnO_4$-treated fabrics were treated with either oxalic acid (8 g/l) or citric acid (10 g/l) at 85 °C for 30 min. Dependence of whiteness index, yellowness index, water absorbency and tensile strength of the so treated fabrics on the duration of $KMnO_4$ treatment is shown in Table 2. Obviously, the duration of $KMnO_4$ exerts a significant effect on the whiteness index irrespective of the acid used, the whiteness index increases with both acids by prolonging the time of $KMnO_4$ treatment from 5 to 20 min then marginally decreases thereafter.

Enhancement of the whiteness by the $KMnO_4$ treatment time is a manifestation of allowing longer contact time for formation of MnO_2. However, for a given time the whiteness index obtained with the $KMnO_4$–oxalic acid system is far greater than that for $KMnO_4$–citric acid system, in accordance with the above results and could be explained on similar lines. Within time range of 5–20 min the yellowness index decreases; minimum values of the latter are observed at 20 min (Table 2). Further prolongation of the time is meaningless because the whiteness index acquires higher values in addition to substantial decrement in tensile strength. Indeed, the tensile strength decreases by increasing duration of $KMnO_4$ treatment indicating progressive molecular degradation. Time of water absorbency; decreases from 2 seconds to less than 1 second after 10 and 20 min treatment in case of $KMnO_4$–oxalic acid system and $KMnO_4$–citric acid system respectively. Results of yellowness index, tensile strength and absorbency advocate the advantage $KMnO_4$–oxalic acid system over $KMnO_4$–citric acid system as far as the time factor of $KMnO_4$ treatment is considered.

3.4. Temperature of $KMnO_4$ treating bath

Table 3 shows the effect of temperature of the $KMnO_4$ treatment on whiteness index, yellowness index, absorbency and tensile strength of the Linen fabric after the latter was subjected to treatment with either oxalic or citric acid. As is evident whiteness index increases significantly upon raising the temperature of $KMnO_4$ bath from 25 °C to 90 °C. This range of temperature acts also in favor of the yellowness index which decreases substantially. Furthermore, water absorbency is improved by elevating the temperature from 25 to 90 °C; meanwhile the tensile strength decreases. These observations are realized with both $KMnO_4$–oxalic acid and $KMnO_4$–citric acid systems; but with the certainty that the former system is more advantageous in terms of better fabric properties within the range studied. It is as well to emphasize that the higher bleaching effect obtained at higher temperatures calls for greater MnO_2 deposition inside the fabrics. It is understandable that MnO_2 intermediate is reduced to Mn^{II} by the acid and produces oxygen atoms available for bleaching as detailed in the aforementioned mechanism.

3.5. Optimization of $KMnO_4$ treatment

Optimum conditions for $KMnO_4$ treatment as a prerequisite for bleaching linen fabric using $KMnO_4$–acid system can be formulated through a close examination of Tables 1–3. A balance among the technical properties studied recommends the following conditions: [$KMnO_4$], 5 g/l; time of $KMnO_4$ treatment, 20 min; and temperature of treatment 60 °C; pH of the $KMnO_4$ solution, 4; Material to liquor ratio, 1:30.

3.6. Acid concentration

After being treated with $KMnO_4$ under the optimum conditions outlined above, the MnO_4-contain linen fabric was subjected to different concentrations of either oxalic acid or citric acid. The acid acts upon the deposited MnO_2 via reduction with creation of atoms of oxygen available of bleaching as described in the mechanism postulated in the foregoing paragraphs.

Table 4 shows the effect of concentrations of oxalic acid and citric acid on major technical properties of linen fabrics reacted thereupon, that is, bleached, by the $KMnO_4$–acid systems. Evidently, increasing the concentration of oxalic acid from 6 to 10 g/l is accompanied by significant enhancement in the whiteness index and yellowness index i.e. the whiteness index increases and the yellowness index decreases. Absorbency is so excellent that a drop of water on the fabric disappears completely in less than 1 second. Similar situation is encountered with citric acid, but at a concentration of 8 g/l. Concentrations higher than 10 g/l oxalic acid and 8 g/l citric acid adversely affect the whiteness index and yellowness index. This suggests that the oxidizing bleaching species loose much of their action through termination of free radicals and/or combination of the oxygen atoms due to a abundance of such species at higher acid concentrations.

Table 4 depicts that the tensile strength of the bleached linen fabric sample decreases by increasing the concentration of citric acid within the range studied though above 8 g/l the decrease becomes much less. The same is the case with oxalic acid but the decrease in tensile strength is only significant at oxalic acid concentration of 10 g/l and above. This could be associated with differences between the two acids with respect to the number of free radicals,

Table 2
Effect of time of $KMnO_4$ treatment on major technical properties of linen fabric.

Time (min)	Oxalic acid[a]				Citric acid[a]			
	Absorbency (sec)	Whiteness index	Yellowness index	Tensile strength (kg.f)	Absorbency (s)	Whiteness index	Yellowness index	Tensile strength (kg.f)
5	2	21.43	17.38	91	3	23.22	16.96	84
10	<1	23.94	16.42	82	2	26.94	15.46	69
20	<1	36.88	10.90	75	<1	29.48	13.98	63
30	<1	35.02	12.00	59	<1	28.10	14.12	58
Blank*	5	−43	–	95	5	−43	–	95

[a] Acid bath—citric acid: 8 g/l; oxalic acid: 10 g/l; temperature 85 °C; time: 30 min.
* Blank means scoured linen fabric. Conditions used: for $KMnO_4$ bath—$KMnO_4$: 5 g/l; temperature: 90 °C; pH 4; Material to liquor ratio 1:30.

Table 3
Effect of temperature of $KMnO_4$ treatment on major technical properties of linen fabric.

Temperature (°C)	Oxalic acid[a]				Citric acid[a]			
	Absorbency (s)	Whiteness index	Yellowness index	Tensile strength	Absorbency (s)	Whiteness index	Yellowness index	Tensile strength
25	5	16.31	19.14	85	6	15.00	18.67	79
60	2	30.45	14.18	77	3	25.00	16.48	72.5
90	<1	36.88	10.90	75	<1	29.48	13.98	63
Blank*	5	−43	–	95	5	−43	–	95

[a] Acid bath—citric acid: 8 g/l; oxalic acid: 10 g/l; temperature: 85 °C; time: 30 min.
* Blank means scoured linen fabric. Conditions used: for $KMnO_4$ bath—$KMnO_4$: 5 g/l; pH 4; time: 20 min; material to liquor ratio 1:30.

their life time and ability to attack the linen cellulose through these free radicals and/or oxygen atoms created as per (Eq. (7) or (8)). The ability of $KMnO_4$–acid system to produce atoms of oxygen would rely on the reducing power of the acid. Current results suggest that citric acid seems to have greater reducing power than does oxalic acid.

3.7. Effect of temperature of the acid bath

MnO_4-containing linen fabric samples were immersed in the acid bath at different temperatures. Acids used include oxalic acid and citric acid. As is clear from Table 3, the effect of raising the acid bath temperature from 30 to 90 °C is to bring about significant improvement in whiteness index, yellowness index and water absorbency and, on the contrary, noticeable decrease in tensile strength particularly with citric acid.

The above consequences of temperature could be associated with the favorable effect of temperature on: (a) swellability of the linen fabric, (b) creation of different free radical species, (c) production of atoms of oxygen via reduction of MnO_2 with the acid, (d) removal of impurities and coloring materials particularly the hydrophobic ones, (e) depolymerization of linen cellulose via acid hydrolysis and/or oxidation via free radical attack on the glucosidic bonds of the cellulose chain and, (f) individual combination of free radicals as well as oxygen atoms independently at higher amounts of both.

3.8. Ultrasound assisted acid treatment in $KMnO_4$-acid bleaching

Previous studies (Ilker Mistik & MÜge YÜkseloglu, 2005) disclosed that faster bleaching at lower temperatures with almost twice the whiteness index of the original cotton materials could be achieved upon ultrasonic-hydrogen peroxide bleaching process. With the latter, the time is shortened to 1/3 of the conventional hot bleaching (90 °C) and the temperature reduced to 40 °C. Ultrasonic bath of 20 kHz and 205 W was used. Also reported was (Basto, Tzanov, & Paulo, 2007) a study concerning the potential of using ultrasound to enhance the bleaching efficiency of laccase enzyme on cotton fabrics. Ultrasound of low intensity (7 W and 20 kHz) at a relatively short time (30 min) seems to act in a synergetic way with the enzyme in the oxidation/removal of the natural coloring matters of cotton at 50 °C. The increased bleaching effect could be attributed to improved diffusion of the enzyme from the liquid phase to the fiber surface throughout the cotton structure. Furthermore, previous reports (Abou-Okeil, El-shafie, & El-Zawahry, 2010) described the use of power ultrasonic (26 kHz, 180 W) as a possible effective technique for improving the bleaching of linen fabric with a combined laccase, hydrogen peroxide bleaching process. The results indicated that ultrasound at 80 °C for 30 min constitute the basis of an effective technique in improving the whiteness index of enzymatically scoured linen fabric, with acceptable tensile strength compared to the conventional bleaching process.

Table 4
Effect of concentration in the acid bath of oxalic and citric acids on major technical properties of linen fabrics.

Concentration (g/l)	Oxalic acid[a]				Citric acid[a]			
	Absorbency (s)	Whiteness index	Yellowness index	Tensile strength (kg.f)	Absorbency (s)	Whiteness index	Yellowness index	Tensile strength (kg.f)
6	4	26.19	15.30	79	4	17.38	17.19	72
8	3	27.02	14.64	78	<1	29.48	13.98	63
10	<1	36.88	10.90	75	<1	18.22	18.14	61
12	<1	17.85	18.75	60	<1	18.72	17.49	59
Blank*	5	−43	–	95	5	−43	–	95

[a] Acid bath—temperature: 85 °C; time: 30 min. Conditions used: for $KMnO_4$ bath—$KMnO_4$: 5 g/l; pH: 4; time: 20 min; temperature: 90 °C; Material to liquor ratio 1:30.
* Blank means scoured linen fabric.

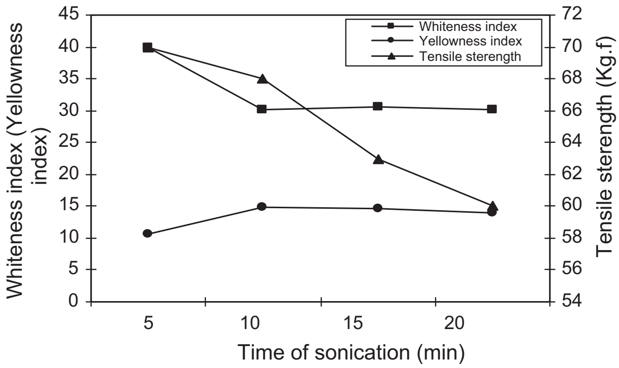


Fig. 1. Effect of temperature of the acid bath of oxalic acid on major technical properties of linen fabric Conditions used: (1) for $KMnO_4$ bath—$KMnO_4$: 5 g/l; pH: 4; time: 20 min; temperature: 90 °C, Material to liquor ratio 1:30. (2) for acid bath—oxalic acid: 10 g/l; time: 30 min.

In the present work, MnO_2-containing linen fabric was subjected to acid bath treatment under the action of ultrasound (as described in the experimental section) at 60 °C for different durations ranging from 5 to 30 min. After being washed and dried, the so treated linen fabrics were monitored for major technical properties. The results obtained are given in Figs. 1 and 2.

The first glance of the results (Fig. 1) reveals that a whiteness index as high 39.97, yellowness 10.75 and water absorbency in less than 1 second could be achieved after acid treatment assisted by ultrasound for only 5 min at 60 °C. Under these conditions the tensile strength exhibits a value of 70 kg. Longer time of treatment with oxalic acid assisted by ultrasound is not advisable because the said properties are deteriorated. In contrast, citric acid treatment assisted by ultrasonic (Fig. 2) brings about lower whiteness index 30.84 and lower tensile strength 60 kg after citric acid treatment assisted by ultrasound for 10 min. Water absorbency (less than 1 second) and yellowness index 10.27 are comparable with those of oxalic acid treatment aided by ultrasound.

The above findings signify clearly the advantages of the ultrasound as a clean environmentally friendly means for conducting the bleaching of linen fabrics at lower temperatures and shorter time; in accordance with the literature (Simona & Le Marechal, 2005). Meanwhile the bleaching fabrics acquire comparable; if not superior, technical properties when compared with fabrics bleached with the same system but without the ultrasound. The same holds true when the comparison is made against conventionally bleached linen fabrics as will be shown latter.

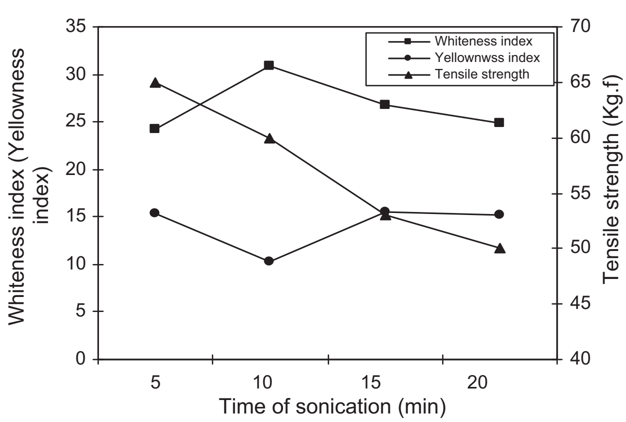


Fig. 2. Effect of temperature of the acid bath of citric acid on major technical properties of linen fabric conditions used: (1) for $KMnO_4$ bath—$KMnO_4$: 5 g/l; pH: 4; time: 20 min; temperature: 90 °C, Material to liquor ratio 1:30. (2) for acid bath—citric acid: 8 g/l; time: 30 min.

The action of ultrasound is attributed to ultrasonic cavitations (Fakin et al., 2006). Cavitation is the formation and violent collapse of small bubbles or voids in the liquid as a result of pressure changes. This occurs when longitudinal waves propagate through the liquid. Cavitation causes several chemical and mechanical effects, such as dispersing, degassing, formation of free ions or radicals and intense agitation of liquid (Fakin et al., 2006) and as a result, accelerating the $KMnO_4$-acid bleaching process which involves the reduction scheme suggested by Eqs. (1)–(15) in the aforementioned bleaching mechanism. The exposure of water to ultrasound results in local hot spots as a consequence of the formation, growth and collapse of cavity bubbles containing entrapped gases and vapors of the surrounding water (Tezcanli-GÜyer & Ince, 2004). At collapse, chemical reactivity is initiated through thermolytic decomposition of bubble contents into free radical species, and/or through free radical oxidation of dissolved solutions at the gas–liquid interface or the bulk liquid (Ince, Tezcanli, & Belen Apikyan, 2000; Joseph, Destaillats, Hung, & Hoffmann, 2000). The chain of reactions occurring during sonication of pure water is represented by Eqs. (9)–(11). If the solution is saturated with oxygen, additional radicals are produced in the gas phase (Fakin et al., 2005)]. This is represented by Eqs. (12) and (13) as given in the bleaching mechanism.

Notably the formation of (•OH) hydroxyl radical using $KMnO_4$-acid system and ultrasound system enhance the bleaching process, and as a result of ultrasound energy the radical formation mechanism (Eq. (8)) as well as termination reaction (Eq. (10)) which, in turn, produces atoms of oxygen (Eq. (11)) in $KMnO_4$-acid bleaching would certainly shorten the time of bleaching. That is, free radicals in combination with oxygen atoms are responsible for bleaching in shorter time as previously predicted under the aforementioned bleaching mechanism. The observed decrease in fiber strength could be associated with the effect of ultrasound on degradation of macromolecules in the amorphous region of treated linen. Such a change in the amorphous region may be accompanied by an initial slight reduction in the crystallinity. Once this is the case, a reduction in interfacial binding strength between the crystals and amorphous regions would take place and contribute in the decrement of tensile strength.

3.9. Bleaching using $KMnO_4$-acid systems with and without ultrasound vis-à-vis conventional method

Scoured linen fabrics were bleached as per the following systems: (1) $KMnO_4$–oxalic acid system, (2) $KMnO_4$–citric acid system (3) $KMnO_4$–oxalic assisted by ultrasound system (4) $KMnO_4$–citric acid assisted by ultrasound system and, (5) conventional H_2O_2 bleaching system. (6) Ultrasound H_2O_2 bleaching system Fabrics obtained with the six systems are evaluated for whiteness index, yellowness index, water absorbency and tensile strength. Results of these investigations are shown in Fig. 3.

The results (Fig. 3) signify that all the bleaching systems examined give fabrics with water absorbency less than one second indicating the ability of these systems to remove all types of impurities particularly the hydrophobic impurities. The use of ultrasound along with $KMnO_4$–oxalic acid and $KMnO_4$–citric acid systems enhances the bleaching effect to a great extent when compared with both systems without ultrasound as well as with the conventional H_2O_2 system. This is evidenced by the values of whiteness (39.97 and 30.84) and yellowness index (10.75 and 10.27) for fabrics bleached with $KMnO_4$–oxalic acid and $KMnO_4$–citric acid systems respectively. These values are against whiteness indexes of 25.48, 33.73, 36.88 and 29.48 for fabrics bleached using the conventional system, ultrasound/H_2O_2 system, $KMnO_4$–oxalic acid system and $KMnO_4$–citric acid respectively. Keeping in mind that bleaching by ultrasound/H_2O_2 system exhibits little much higher value for whiteness index (33.73) than $KMnO_4$–citric acid assisted

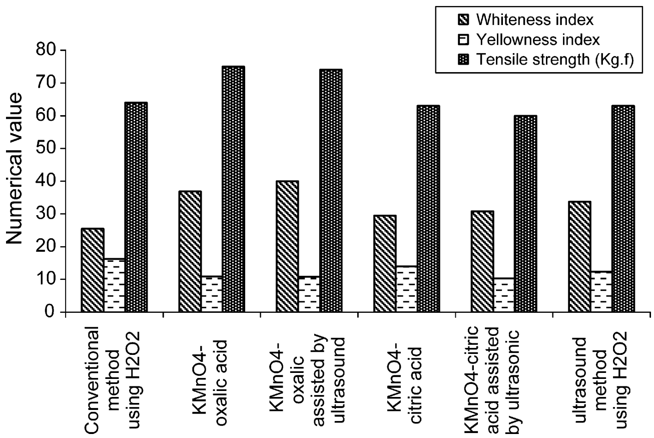


Fig. 3. Comparison among the bleached linen fabrics produced using $KMnO_4$-acid systems with and without ultrasound and conventional and ultrasound H_2O_2 bleaching.

by ultrasound system with longer time of treatment (60 min) against (10 min). At the same time fabric bleached using ultrasound assisted $KMnO_4$-oxalic acid system exhibits the highest tensile strength (75 kg) and that bleached using ultrasound assisted $KMnO_4$-citric acid system the least (60 kg) while those bleached using the conventional H_2O_2 system (64 kg), the ultrasound bleaching using H_2O_2 (63 kg) and $KMnO_4$–citric acid system (63 kg) stands in mid way position.

Based on the above, the use of ultrasound assisted $KMnO_4$-oxalic acid system is by far the most appropriate system for bleaching linen fabrics as the latter acquire excellent water absorbency, higher improved whiteness (high value) and yellowness (low value) indexes and very acceptable tensile strength. Considering the technical properties examined, the six systems under investigation would follow the order: ultrasound/$KMnO_4$–oxalic acid > $KMnO_4$–oxalic acid > ultrasound/H_2O_2 method > ultrasound/ $KMnO_4$–citric acid > $KMnO_4$–citric acid > conventional H_2O_2 method. This order is rather a manifestation of the differences among these bleaching systems with respect to generation of free radicals and atoms of oxygen and the onset of both on the impurities and the cellulose of the linen fabric.

4. Conclusion

Bleaching of scoured linen fabric with $KMnO_4$-acid system comprises two distinct steps. The first step involves treatment of linen fabric with $KMnO_4$ solution at pH 4 to produce MnO_2 in the interior of the fabric. In the second step the MnO_2 deposited on the fabric is acted upon via reduction by oxalic acid or citric acid. The ultrasound is introduced in the acid treatment step to accelerate generation of oxidizing species, namely, free radicals and atoms of oxygen: both species are available for bleaching. The bleached linen fabrics were monitored for whiteness and yellowness indexes, water absorbency and tensile strength. These properties are dependent upon the $KMnO_4$ concentration and temperature and time of $KMnO_4$ bath. Optimization studies lead to the following conditions: [$KMnO_4$], 5 g/l at pH 4 and 90 °C for 20 min using material to liquor ratio 1:30. Similarly, the optimal conditions for oxalic acid treatment with and without ultrasound assistance are: [oxalic acid], 10 g/l at 85 °C for 30 min. The same conditions are valid for citric acid but at a concentration of 8 g/l. Studies concerning the bleaching effect among the different systems examined bring into focus the following order:

Ultrasound assisted $KMnO_4$–oxalic acid > $KMnO_4$–oxalic acid > ultrasound/H_2O_2 method > ultrasound assisted $KMnO_4$–citric acid > $KMnO_4$–citric acid > conventional H_2O_2 method.

It is as well to emphasize that the ultrasound assisted $KMnO_4$–oxaic acid system is by far the most appropriate for bleaching linen fabrics. The latter display excellent water absorbency highly improved whiteness index (with greater value) and very acceptable tensile strength. The introduction of ultrasound in the acid treatment shortens the time from 30 min to 5 and 10 min in cases of oxalic acid and citric acid, respectively, and decreases the temperature from 85 °C to 60 °C for both acids.

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