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An effective redox system for bleaching cotton cellulose

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ABSTRACT

An effective sodium chlorite/potassium permanganate bleaching system was used to bleach cotton fabric without severe loss in the fabric's mechanical properties. The bleaching process based on depositing Mn^{III} on the fabric surface followed by treating the fabric with sodium chlorite solution. Parameters governing the bleaching efficiency, like potassium permanganate concentration, sodium chlorite concentration and bleaching bath temperature were studied. The bleached fabrics were fully characterized by measuring their whiteness index, carboxyl and carbonyl contents, percent loss in fabric weight and tensile strength. The obtained results reveal that bleached cotton fabric with satisfactory whiteness index and reasonable tensile strength can be obtained by soaking the fabric, at 50 °C in potassium permanganate solution (0.01 N), using material to liquor ratio of 1:10. The fabric is then rinsed with distilled water, squeezed and introduced to bleaching bath containing 5 g/l sodium chlorite and 1 g/l non-ionic wetting agent using a material to liquor ratio of 1:10.

1. Introduction

The processing of raw cotton in order to improve its performance in further finishing stages consists of three consecutive steps: desizing, scouring and bleaching. The scouring of the cotton fabrics is a process, which aims to improve the absorbency of textile materials, removing from the fibers the non-cellulosic natural matter. Natural fibers and fabrics even after scouring still contain naturally occurring coloring matter. This yellowish and brown discoloration may be related to flavones pigments present naturally in the fiber. The climate, soil, drought and frost can also cause various degrees of yellowness. Discoloration may also come from dirt, dust, and insects or from harvesting or processing equipments in the form of oils and greases. The objective of bleaching is to produce white fabrics by destroying the coloring matter with the help of bleaching agents with minimum degradation of the fiber. The bleaching agents either oxidize or reduce the coloring matter which is washed out and whiteness thus obtained is of permanent nature. Chemical bleaching of textile fibers is further aided by addition of optical brighteners.

Technology for preparation of cellulosic fiber materials aiming to improve their performance comprises several consecutive operations, i.e. desizing (Abdel-Halim et al., 2011a; Abdel-Halim, El-Rafie, & Al-Deyab, 2011b; Ahlawat, Dhiman, Battan, Mandhan, & Sharma, 2009; Bae et al., 2006; Peng et al., 2010), scouring (Abdel-Halim, Fahmy, & Fouda, 2008; Abdel-Halim, Konczewicz, Zimniewska, Al-Deyab, & El-Newehy, 2010a; El Shafie, Fouda, & Hashem, 2009) and bleaching (Abdel-Halim, Abdel-Mohdy, Al-Deyab, & El-Newehy, 2010b, Abdel-Halim & Al-Deyab, 2011a; Abdel-Halim, 2012a, 2012b; Hashem, El-Bisi, Sharaf, & Refaie, 2010; Hebeish et al., 2009; Hou, Zhang, & Zhou, 2010; Ibrahim, Sharaf, & Hashem, 2010). The whitening of textiles is achieved with different oxidizing or reducing agents, capable of destroying the natural pigments and matter present in the fibers. Nowadays hydrogen peroxide, due to its biodegradability, almost entirely replaced the conventional chlorine oxidizing chemicals (Abdel-Halim & Al-Deyab, 2011b, 2011c, 2011d; Spirro & Criffith, 1997). Hydrogen peroxide precursors, such as perborates and percarbonates are incorporated in a major part of commercially available detergent compositions. Alternatively, hydrogen peroxide could be produced enzymatically by glucose oxidase catalyzed conversion of glucose in the presence of oxygen in aqueous solutions (Aly, Moustafa, & Hebeish, 2004; Bajpai, Anand, & Bajpai, 2006; Tzanov, Costa, Gübitz, & Cavaco-Paulo, 2002).

Fabrics made of cotton are very comfortable to wear and easy to dye because cellulose has excellent properties such as higher water and moisture absorbency. For these reasons, the apparel industry is predominantly cotton based, and the share of cotton in total fiber consumption is about 50%. Cotton is composed almost entirely of cellulose (90–96% based on weight of fibers). The impurities in cotton fiber range from 4% to 10%. The overall composition of raw cotton fibers depends on its type, origin, fibers maturity, weathering and agricultural conditions

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(Mandal & Venugopalan, 2005; Stathakos, Gemtos, Tsatsarelis, & Galanopoulou, 2006; Wolf & Hadas, 1984). The impurities include protein (1.0–2.1%), wax (0.4–1.7%), ash (inorganic salts) (0.7–1.8%), pectin (0.4–1.9%) and others (resins, pigments, hemicelluloses) (1.5–2.5%) (Gallo & Almirall, 2009; Karmakar, 1999; Plant, Kerby, Zelinski, & Munk, 1998). The yellowish or brown coloration of the cotton fiber is related to the protoplasmic residues of protein and the flavones pigments of cotton flowers (Abidi, Cabrales, & Hequet, 2010; Ghule, Chen, Tzing, Lo, & Ling, 2004). With the exception of natural coloring matters that may be removed by bleaching using certain oxidants, many other impurities are removed by alkali treatment in scouring stage. The latter in common practice involves boiling the cotton in sodium hydroxide (2–5%) for 1 h (Chung, Lee, & Choe, 2004; Degani, Gepstein, & Dosoretz, 2004; Tanapongpipat, Khamman, Pruksathorm, & Hunsom, 2008). Hydrogen peroxide is a well known environmentally safe bleaching agent for cotton fabrics. However, bleaching of cotton based fabrics with hydrogen peroxide requires alkaline medium (normally NaOH), stabilizer and either high temperatures or long treatment times (Abou-Okeil, El-Shafie, & El Zawahry, 2010). After bleaching and before dying, large amount of water is required for washing the residual non decomposed hydrogen peroxide and the residual alkali (Abou-Okeil et al., 2010; Götz, Duschner, White, & Klukowska, 2007). It is thus desirable to use bleaching systems that operate well at lower temperatures, shorter reaction times and/or using lower chemical charges than current, without causing unacceptable damage to textile fibers.

Sodium chlorite on decomposition produces a strong oxidizing gas known as chlorine dioxide. The lower the pH values and the higher the temperature (above 70 °C) of bleach bath, the greater is the speed of decomposition (Hubbell & Ragauskas, 2010). The rate of chlorine dioxide formation is proportional to the concentration of sodium chlorite in the solution. Chlorous acid ($HClO_2$) that is formed is unstable and decomposes to chlorine dioxide (ClO_2) which is the active species so far as bleaching is concerned. Maximum chlorine dioxide is formed between pH 2.5 and 3.0. In the absence of metal ions and textiles, the rate of formation of chlorine dioxide approximately doubles for each 0.4-pH drop, in the 3.0–5.0 range, at 85 °C. Addition of an acid such as formic, acetic or phosphoric acid is recommended so that pH lies between 3 and 5. If the pH drops below 3.0, cellulosic fiber is severely damaged because weak acid ($HClO_2$) and strong acid (HC1) are formed which hydrolyze the cellulose. On the other hand, the loss of oxygen evolution from hot chlorite solution when cellulosic fiber is added also suggests that chlorite ion rather than chlorous acid is responsible for bleaching (Eqs. (1)–(3)) (Tamura, Hirota, Saito, & Isogai, 2010).

$$2NaClO_2 + H_2SO_4 \rightarrow 2HClO_2 + Na_2SO_4 \quad (1)$$

$$HClO_2 \rightarrow ClO_2^- + H^+ \quad (2)$$

$$HClO_2 \rightarrow HCl + 2O \quad (3)$$

Aqueous sodium chlorite solutions, which are stable under alkaline conditions, are to be activated by acidification. Activation with strong acid produces toxic corrosive chlorine dioxide gas. It is thus necessary to control its rate of evolution. Technical developments have been linked mainly to control the chlorine dioxide evolution (Hirota, Tamura, Saito, & Isogai, 2009). In practice this is generally achieved by controlling the temperature and pH by addition of buffers in the bleach bath. This can be avoided by addition of weak acid (which forms a buffer with the alkali in the chlorite) or a mixture of weak acid and its salt with a strong base. Some auxiliary products function by giving a slow development of acidity on heating or long storage at ambient temperatures. Activation with persulfates above pH 7 and aldehyde at pH 3–7 (López et al., 2001) have been proposed and also activation by organic acid esters such as ethyl lactate (1–3 g/l) with addition of sodium nitrate (1–3 g/l) to inhibit corrosion (Bäck & Singh, 2004) is possible. Sodium hydrogen orthophosphate (NaH_2PO_4) and sodium formate which produce acid when the liquor is heated are also suggested as buffers. Organic esters such as diethyl tartarate which hydrolyses to give tartaric acid, or sodium chloroacetate which liberates hydrochloric acid and glycolic acid during steaming, have also been suggested as buffers. Other alternatives are the use of either special auxiliary products which limit chlorine dioxide evolution, for example, foam formation on the bleach liquor surface or other chemicals capable of trapping chlorine dioxide chemically.

The present work aims at finding out the most appropriate conditions to bleach cotton in one step process using the powerful sodium chlorite/potassium permanganate redox system, keeping in mind the quality of the bleached fabric, the cost of the bleaching process and its environmental impact.

2. Experimental

2.1. Materials

Plain weave 100% cotton fabric was supplied by Misr Company for Spinning and Weaving, Mehalla El-Kobra, Egypt. The fabric specifications were as follow: fabric weight, 150 g/m^2, weft 30 yarn/cm, warp 36 yarn/cm. The fabric warps were tested for sizing agent and the test showed starch-based sizing agent.

2.2. Chemicals

Sodium chlorite was supplied by BDH. Potassium permanganate; potassium iodide and sodium thiosulfate were supplied by Sigma–Aldrich. Sulfuric acid was supplied by Merk.

2.3. Bleaching process

Cotton fabric samples (20 g each) were soaked in potassium permanganate solutions (0–0.16 N) for 15 min at 50 °C, where manganese dioxide is deposited on the fabric surface. The fabric samples are removed from the permanganate solution, rinsed several times with distilled water to remove the excess manganese dioxide and then squeezed. The potassium permanganate-treated cotton samples were then put in a solution containing sodium chlorite (5 g/l) and wetting agent, Lavotan DSU (1 g/l) using a material to liquor ratio of 1:10. The treatments were carried out at different temperatures 50–95 °C and pH 7. Sodium chlorite decomposition was monitored by withdrawing and analyzing samples from the bleaching liquor at different time intervals (Vogel, 1961). After bleaching, the cotton fabric samples were thoroughly washed with hot and then cold water and finally dried at ambient conditions. The chemical and physical properties of the treated fabrics were evaluated via measuring the carboxyl and carbonyl contents, whiteness index, tenacity, and percent loss in fabric weight.

2.4. Testing and analysis

2.4.1. Weight loss

Fabric weight loss was calculated on the basis of dry weight using the following formula:

$$\%\,\text{weight loss} = \frac{W1 - W2 \times 100}{W1}$$

where $W1$ and $W2$ are the dry weights of the fiber before and after bleaching treatment, respectively.

2.4.2. *Carboxyl and carbonyl contents*

Carbonyl and carboxyl contents of bleached cotton fabric were measured according to the following reported methods, respectively (Mattisson & Legendre, 1952; Nelson & Tripp, 1953).

2.4.3. *Degree of whiteness*

The degree of whiteness of bleached cotton samples, expressed as whiteness index was measured using a Hunterlab Reflectometer (Model D25 M/L-2). The WI was calculated in terms of CIE Y (green) and (blue) reflectance components using the formula (ASTM Method E31373).

$$W.I. = \frac{4Z}{1.18} - 3Y$$

where Y and Z are the readings of the device.

2.4.4. *Tensile strength*

The tensile strength of cotton fabrics was measured according to the ASTM strip test (ASTM Test Method).

3. Results and discussion

3.1. *Tentative mechanism*

When cotton fabric is treated with potassium permanganate solution, substantial amount of MnO_2 is deposited on the cotton fabric. Once this occurs radical species are formed by virtue of reduction of M^{IV} to either Mn^{III} or Mn^{II} (Eqs. (4) and (5))

$$Mn^{IV} + H_2O \rightarrow Mn^{III} + H^+ + HO^\bullet \tag{4}$$

$$Mn^{III} + H_2O \rightarrow Mn^{II} + H^+ + HO^\bullet \tag{5}$$

The hydroxyl free radicals activate the chlorite ions and chain reactions can take place and thus producing different active species responsible for cotton fabric bleaching. These chain reactions are exemplified by Eqs. (6)–(10).

$$ClO_2^- + HO^\bullet \rightarrow ClO^- + HO_2^\bullet \tag{6}$$

$$ClO_2^- + HO^\bullet \rightarrow ClO_2^\bullet + HO^- \tag{7}$$

$$2ClO_2^- + ClO^- \rightarrow ClO_3^- \tag{8}$$

$$ClO_2^\bullet + ClO^- \rightarrow ClO_2^- + ClO^\bullet \tag{9}$$

$$ClO^\bullet + ClO^- + HO^- \rightarrow Cl_2 + O_2 + HO^\bullet \tag{10}$$

The bleaching effect is also expected to depend upon the pH of the bleaching bath as follows:

(a) In acidic media (Eqs. (11) and (12))

$$Mn^{IV} + RH \rightarrow Mn^{III} + H^+ + R^\bullet \tag{11}$$

$$Mn^{III} + RH \rightarrow Mn^{II} + H^+ + R^\bullet \tag{12}$$

where RH is an acid. Like HO radicals, the free radicals R can react with the chlorite ions thereby initiating chain reactions exactly as those suggested by Eqs. (6)–(10). In addition, the chlorite ions dissociate in acidic media as follows (Eqs. (13)–(15))

$$4ClO_2^- + 2H^+ \rightarrow 3ClO_2 + Cl^- + 2HO^- \tag{13}$$

$$3ClO_2^- \rightarrow 2ClO_3^- + Cl^- \tag{14}$$

$$2ClO_3^- \rightarrow 2Cl^- + 3O_2 \tag{15}$$

Hydrochloric acid is probably formed via reaction of the hydrogen ion of Eqs. (4), (5), (11) and (12) with the chlorine ion of Eqs. (13)–(15) and this hydrochloric acid would accelerate the decomposition of sodium chlorite.

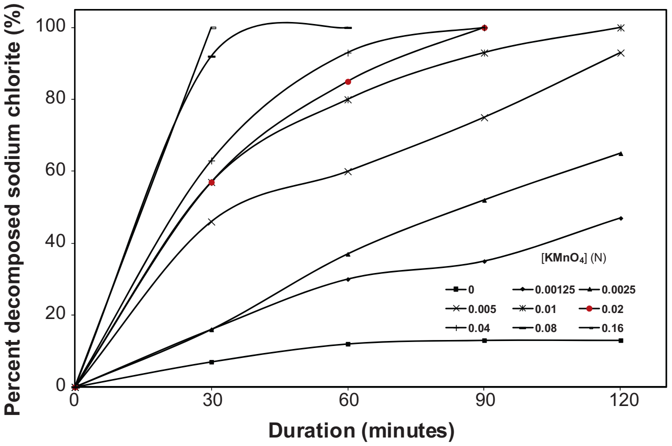

Fig. 1. Effect of potassium permanganate concentration on sodium chlorite decomposition. Soaking in $KMnO_4$ solution using material to liquor ratio 1:10 for 1 min at 50 °C then rinsing and squeezing; [$NaClO_2$], g/l; M/L ratio, 1:10; Lavotan DSU, g/l; bleaching bath temperature, 95 °C; bleaching duration, 12 min; initial pH 7.

3.2. *In alkaline media*

At higher pH values (alkaline media), the chlorite ions may be decomposed as in Eq. (16) to give chlorate ions and oxygen.

$$6ClO_2^- \rightarrow 2ClO_3^- + 4Cl^- + 3O_2 \tag{16}$$

3.3. *Effect of potassium permanganate concentration on sodium chlorite decomposition*

In order to investigate the catalytic effect of potassium permanganate on cotton fabric bleaching with sodium chlorite, several trials have been carried out using aqueous sodium chlorite solution 5 g/l together with different concentrations of potassium permanganate, using a material to liquor ratio of 1:10 and pH 7 at 70 °C. Fig. 1 shows the extent and rate of sodium chlorite decomposition upon bleaching cotton fabrics with aqueous solution containing 5 g/l sodium chlorite and different concentrations of potassium permanganate, namely 0–0.16 N. It is evident from the results that the percent decomposed sodium chlorite is significantly higher in presence than in absence of potassium permanganate and that at a given time, the rate of decomposition increases by increasing potassium permanganate concentration used for pretreatment of the cotton samples. This could be attributed to the amount of liberated acid, which catalyzes sodium chlorite decomposition. In addition, it is clear from the figure that 100% sodium chlorite decomposition needs either long time at low potassium permanganate concentration or shorter time at higher potassium permanganate concentration. The amount of toxic chlorine dioxide evolved during the bleaching process is marginal compared with the conventional sodium chlorite bleaching methods. However, whiteness index and tensile strength measurements (Table 1) showed that 0.01 N is the optimum potassium permanganate concentration, that at this concentration, sodium chlorite decomposes gradually within reasonable bleaching duration (120 min) giving rise to acceptable whiteness index (63.5) and good tensile strength (28.3 g/tex). Using lower potassium permanganate concentrations (0.00125–0.005 N) leads to incomplete sodium chlorite decomposition within reasonable bleaching time, which will not lead to remarkable improvement in the whiteness index or the tensile strength. On the other hand, using higher concentrations of potassium permanganate (0.02–0.08 N) leads to faster sodium chlorite decomposition (within the first 60 min) and this is reflected in the form of less improvement in the whiteness index or the tensile strength, compared with the case of using 0.01 N potassium

Table 1
Effect of potassium permanganate concentration on chemical and physical properties of cotton fabric.

$KMnO_4$ (N)	Carboxyl content (mequiv./100 g)	Carbonyl content (mequiv./100 g)	Whiteness index	Loss in weight	Tenacity (g/tex)
0	8.9	3.7	25	3.2	34.25
0.00125	9.2	3.7	29	3.7	29.3
0.0025	9.4	4	35	3.8	28.7
0.005	10.9	5	43.16	4.2	28
0.01	12	5	63.5	5	28.3
0.02	11	4.2	39.87	5	31.45
0.04	9.2	4	38.45	4.3	32
0.08	9	3.8	34	3.6	33.88
1.6	8.7	3.2	26	3.3	34.16
Grey cotton	8.5	3	19	–	36.5

Soaking in $KMnO_4$ solution using material to liquor ratio 1:10 for 1 min at 50 °C then rinsing and squeezing; [$NaClO_2$], g/l; M/L ratio, 1:10; Lavotan DSU, g/l; bleaching bath temperature, 95 °C; bleaching duration, 12 min; initial pH 7.

permanganate. Finally, the use of very high potassium permanganate concentration (0.16 N) leads to instant 100% decomposition of Sodium chlorite without imparting any bleaching effect to the cotton fabrics.

3.4. Effect of potassium permanganate concentration on physiochemical properties of bleached cotton fabrics

Table 1 shows the chemical and physical properties of cotton samples bleached using 5 g/l sodium chlorite in combination with different concentrations from potassium permanganate. It is clear from the table that the carboxyl content, carbonyl content, loss in weight and the whiteness index (WI) increase by increasing potassium permanganate concentration during the pretreatment step up to 0.01 N. Further increase above this limit is accompanied by a decrease in the above mentioned properties. However, the reverse holds true with the tenacity of the bleached cotton fabrics. This is logic because as the concentration of potassium permanganate increases up to 0.01 N, the activity of sodium chlorite as oxidizing/bleaching agent improves leading to more removal of non-cellulosic materials (lower tenacity), improvement in carboxyl and carbonyl contents as well as better whiteness index. The decrement in the carboxyl content, carbonyl content, WI, and the increment in the tenacity when cotton fabrics were pretreated with potassium permanganate concentration higher than 0.01 N could be ascribed to faster rate of sodium chlorite decomposition without attacking the coloring matter in cotton fabric. Regardless of the bleaching conditions used, the tenacity of the bleached fabric is lower than that of the unbleached fabric, which could be attributed to degradation of the cellulose fibers as well as removal of some non-cellulosic materials during the bleaching treatment. The percent loss in fabric weight due to this bleaching process does not exceed 5%, which is reasonable compared with the traditional techniques used in cotton bleaching. Taking in mind the rate of sodium chlorite decomposition and its effect on the chemical and physical properties of the bleached cotton fabric, it could be concluded that 0.01 N potassium permanganate represents the optimal concentration needed to activate sodium chlorite during the bleaching process.

3.5. Effect of sodium chlorite concentration on its decomposition percent

Fig. 2 shows the effect of sodium chlorite concentration used for bleaching cotton fabrics on the percent decomposed chlorite. Cotton samples were pretreated with 0.01 N potassium permanganate solution and different concentrations from sodium chlorite, namely, 1, 3, 5, 7 and 9 g/l were used for the bleaching process. Lower sodium chlorite concentrations (1 g/l or 3 g/l) show low percent decomposed sodium chlorite within the reaction time 2 h, maximum 33% in case of using 1 g/l sodium chlorite and maximum 44% in case of using 3 g/l sodium chlorite. This low sodium chlorite decomposition percent at low sodium chlorite concentration is most probably due to low concentration of hydrochloric acid produced as a result of combination of hydrogen ions resulting from reactions 4, 5, 11 and 12 with the chlorine ions resulting from reactions (13) to (15) and accordingly, low hydrochloric acid concentration means low sodium chlorite activation. On the other hand, higher sodium chlorite concentrations (7 g/l or 9 g/l) show very fast sodium chlorite decomposition in the early reaction stage and this is attributed to production of large amounts of hydrochloric acid, which decreases the bleaching medium pH to a very low value, giving rise to very fast sodium chlorite decomposition. Of course, this very fast decomposition of sodium chlorite when increasing its concentration in the bleaching bath to 7 g/l or 9 g/l makes sodium chlorite useless that it decomposes without imparting any bleaching effect to the cotton fabrics and this will be seen very clear in the very low whiteness index value.

3.6. Effect of sodium chlorite concentration on physiochemical properties of bleached cotton fabrics

Table 2 shows the chemical and physical properties of the bleached cotton fabrics. Cotton samples were pretreated with 0.01 N potassium permanganate solution, and different concentrations from sodium chlorite, namely, 1, 3, 5, 7 and 9 g/l were used for the bleaching process. The physical and chemical properties of the

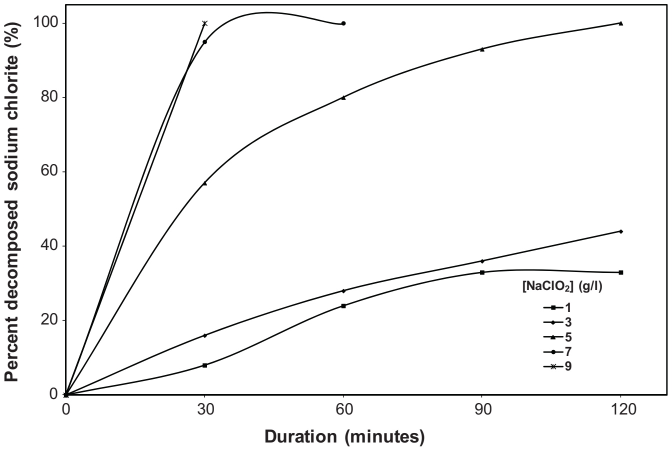

Fig. 2. Effect of sodium chlorite concentration on its decomposition rate. Soaking in 0.01 N $KMnO_4$ solution using material to liquor ratio 1:10 for 1 min at 50 °C then rinsing and squeezing; bleaching with aqueous $NaClO_2$ solution in a M/L ratio, 1:10; Lavotan DSU, g/l; bleaching bath temperature, 95 °C; bleaching duration, 12 min; initial pH 7.

Table 2
Effect of sodium chlorite concentration on chemical and physical properties of cotton fabric.

[$NaClO_2$] (g/l)	Carboxyl content (mequiv./100 g)	Carbonyl content (mequiv./100 g)	Whiteness index	Loss in weight	Tenacity (g/tex)
1	9.3	3.2	27.23	1.95	32.97
3	10.4	4	36.45	2.2	30
5	12	5	63.5	5	28.3
7	8.6	3.7	26.99	1.3	33.76
9	8.7	3.3	22.50	0.8	34.99
Grey cotton	8.5	3	19	–	36.5

Soaking in 0.01 N $KMnO_4$ solution using material to liquor ratio 1:10 for 15 min at 50 °C then rinsing and squeezing; bleaching with aqueous $NaClO_2$ solution in a M/L ratio, 1:10; Lavotan DSU, 1 g/l; bleaching bath temperature, 95 °C; bleaching duration, 120 min; initial pH 7.

Table 3
Effect of reaction temperature on chemical and physical properties of cotton fabric.

Reaction temperature (°C)	Carboxyl content (mequiv./100 g)	Carbonyl content (mequiv./100 g)	Whiteness index	Loss in weight	Tenacity (g/tex)
50	8.7	3.3	22.23	1.5	35
70	9.1	3.8	33.50	3	33.99
80	10.2	4.2	42.35	4.1	30.70
95	12	5	63.5	5	28.3
Grey cotton	8.5	3	19	–	36.5

Soaking in 0.01 N $KMnO_4$ solution using material to liquor ratio 1:10 for 1 min at 50 °C then rinsing and squeezing; [$NaClO_2$], g/l; M/L ratio, 1:10; Lavotan DSU, g/l; bleaching duration, 12 min; initial pH 7.

bleached cotton fabrics give indication about the rate of sodium chlorite decomposition. The low sodium chlorite decomposition percent at low sodium chlorite concentration 1 g/l and 3 g/l led to bad carboxyl content, carbonyl content, whiteness index and loss in weight compared with the case of using 5 g/l sodium chlorite for bleaching. Also in case of using high sodium chlorite concentrations for bleaching (7 g/l or 9 g/l), the situation was worse, that sodium chlorite showed very fast decomposition in the very early stage of the bleaching reaction and the physiochemical properties of the bleached cotton fabrics did not show remarkable improvement compared to the grey cotton fabric. Based on the above, one can conclude that 5 g/l is optimum sodium chlorite concentration for cotton fabric bleaching.

3.7. Effect of bleaching bath temperature on sodium chlorite decomposition

Fig. 3 shows the effect of the bleaching bath temperature on sodium chlorite decomposition, at fixed potassium permanganate concentration (0.01 g/l) and fixed sodium chlorite concentration (5 g/l). The results show that on carrying out the bleaching reaction at 95 °C, sodium chlorite is fully decomposed within 2 h, while on carrying the bleaching at lower temperature, namely 80 °C, 70 °C or 50 °C, maximum 71% of the sodium chlorite decomposed within the time range studied (2 h). The enhancement in sodium chlorite decomposition at high bleaching temperatures (95 °C) is due to the favorable effect of temperature on the free radicals formation, which in turn activates sodium chlorite decomposition (Eqs. (6)–(10)). In addition to the above, high temperature increase the kinetic energy of the molecules and makes cotton fabric more swollen and increases its accessibility, giving rise to faster diffusion of the bleaching agent to the bulk of the fabric.

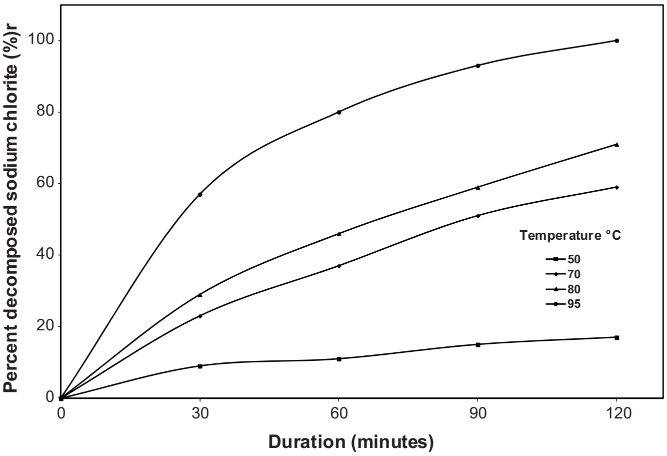

Fig. 3. Effect of reaction temperature on sodium chlorite decomposition. Soaking in 0.01 N $KMnO_4$ solution using material to liquor ratio 1:10 for 1 min at 50 °C then rinsing and squeezing; [$NaClO_2$], g/l; M/L ratio, 1:10; Lavotan DSU, g/l; bleaching duration, 12 min; initial pH 7.

3.8. Effect of bleaching bath temperature on physiochemical properties of bleached cotton fabrics

Table 3 shows the physiochemical properties of the bleached cotton fabric. From the table, it is clear that the carbonyl content, carboxyl content, whiteness index and percent loss in weight increase by raising the bleaching bath temperature. This is because the higher the temperature, the high will be the percent decomposed sodium chlorite and also the higher will be the activity of the oxidizing species in oxidizing the cellulose, improving the whiteness index and carboxyl and carbonyl contents, as well as in removing the non-cellulosic materials, increasing the percent loss in weight. The higher the temperature the higher will be the degradation of the cellulosic chains and the removal of the non-cellulosic materials and accordingly the lower will be the tensile properties of the bleached fabrics. It could be concluded from the above-mentioned results that adequate bleaching action with acceptable tenacity could be obtained when cotton fabrics pretreated with 0.01 N potassium permanganate were coupled with 5 g/l $NaClO_2$ at 95 °C for 120 min using a material to liquor ratio of 1:10.

4. Conclusion

Sodium chlorite/potassium permanganate bleaching system was tried to bleach cotton fabric in one-step process. Different bleaching trials were carried out keeping fixed sodium chlorite concentration and varying other reaction conditions like potassium permanganate concentration (0–0.16 N) and bleaching temperature (50, 70, 80 and 95 °C). The bleaching reaction was monitored by following the percent decomposed sodium chlorite at different time intervals. The obtained results indicate that the higher the concentration of potassium permanganate incorporated to the bleaching medium, the higher is the percent decomposed sodium chlorite at a given bleaching time. Also at a given potassium permanganate concentration, the higher the bleaching time, the higher is the percent decomposed sodium chlorite. The bleached fabrics were fully characterized by measuring their whiteness index, carboxyl and carbonyl contents, percent loss in fabric weight and tensile strength. The obtained results reveal that bleached cotton fabric with satisfactory whiteness index and reasonable tensile strength can be obtained by soaking the fabric at 50 °C in potassium permanganate solution (0.01 N), using M/L ratio of 1:10. The fabric is rinsed with distilled water, squeezed and then introduced to bleaching bath containing 5 g/l sodium chlorite and 1 g/l nonionic wetting agent using a material to liquor ratio of 1:10. These optimum conditions lead to completion of the bleaching process in reasonable duration of 2 h with minimum evolution of harmful chlorine dioxide gas. Lower concentrations of the activator potassium permanganate were found to result in not satisfactory whiteness index due to incomplete decomposition of sodium chlorite, while on the other hand, higher concentrations of the activator potassium permanganate were found to cause very fast sodium chlorite decomposition at early stage of the reaction without imparting any bleaching effect to the cotton fabric.

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