

Study of the Influence of Bleaching Process Time on the Brightness of the De-Inked Waste Paper Pulp Using Hydrogen Peroxide as a Bleaching Agent

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Abstract
This research aims to study bleaching time influence on the brightness level of the de-inked waste paper pulp using hydrogen peroxide as a bleaching agent, and that will be through evaluating how pulp brightness changes within a range of process times. In addition, the kinetics of the bleaching reaction is studied and analyzed.The experiments were conducted using a laboratory pulper designed to simulate the industrial pulpers, but also modified to meet the goals and conditions of the research.The results show that brightness increases with bleaching time, and the optimum time for bleaching process at research conditions was determined at 70 min. It is also found that applying longer times would contribute with only minimum additions on brightness and that do not justify the costs of operating with extended periods. On the other hand, lowering process time below 70 min may result in a considerable decrease in the brightness of the recycled pulp. Here, kinetics shows a significant remaining amount of peroxide after the process ends, which leads to lower brightness and efficiency.
Keywords: Bleaching, Time, Brightness, Hydrogen peroxide.

1. Introduction

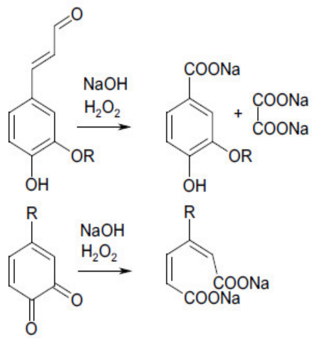
As attention toward recycled fibers has recently increased for ecological and economical reasons, it was necessary to find new ways to improve recycled pulp properties to make them meet the high requirements in paper market. In spite of the application of several processes to remove contaminants from waste paper, producing paper with high optical properties required an additional process. This process is refereed to as Bleaching (1) (2).

Literature review

Bleaching of recycled fibers is defined as a chemical process that aims to brighten the fibers through removing the color caused by residual lignin and other contaminants (3). The color results from the presence of unsaturated chemical structures called chromophores (4), most of which are existed in lignin compounds. The latter is a substance originates from wood, the origin of most paper grades. Specific amount of lignin, differs according to paper grade, remains in paper products after processing the wood in integrated paper mills (5). The mechanism of how chromophores give the pulp a darker color is through absorbing a portion of the light spectrum by means of the conjugated bonds system existed in these structures and reflects the rest which is received by the eye and perceived as dark appearance. A very small amount of chromophores are enough to give the pulp a darker color. By altering the chemical composition of these chromophores, bleaching process aims at producing a brighter pulp (6) (4).

To apply bleaching process, many chemical agents can be utilized. Some of them are oxidative while the others are reductive (7). Among these various compounds, hydrogen peroxide H_2O_2 is considered as the most favorable chemical for the bleaching of waste paper pulp, due to its effectiveness in increasing pulp brightness besides its correspondence with environmental requirements (8) (2). Therefore, in this study, we used this chemical as a bleaching agent.

Hydrogen peroxide reacts in alkaline conditions with chromophores and alters their composition to colorless forms, as shown in the following equations (9):



Bleaching can be performed in one point or more along the processing line of waste paper, but due to brightness reduction triggered by the alkaline conditions in the pulper, hydrogen peroxide is usually added to the pulper itself to compensate this reduction (1). Stabilizing agents, like sodium silicate, are also added to stabilize hydrogen peroxide, as they remove metallic ions that weaken peroxide stability and catalyze its decomposition (7).

In alkaline conditions, bleaching process using hydrogen peroxide is activated by producing the active perhydroxyl anion HO_2^- as shown in the following equation (10):

$$H_2O_2 + OH^- \rightleftharpoons H_2O + HO_2^-$$

Many variables effect bleaching process. In this research we have investigated the influence of the bleaching time upon this process.

Research objective

This research aims to study the influence of bleaching time on the brightness of deinked waste paper pulp using hydrogen peroxide as a bleaching agent, through investigating how this brightness changes with process duration while maintaining other variables constant. In addition, the kinetics of bleaching reaction is examined at research conditions.

2. Materials and devices

- The followings are the materials used in this research:

1- Old corrugated carton OCC
2- Newsprint.
3- Kraft paper.
4- Solid Sodium Hydroxide NaOH, commercial grade - purity 86%.
5- Liquid Sodium silicate Na_2SiO_3, commercial grade - concentration 44%, density 1.525g/cm^3 and SiO_2:Na_2O = 2:1.
6- Hydrogen peroxide solution H_2O_2, commercial grade – concentration 35.8% and density 1.16gr/cm^3.
7- Potassium Permanganate $KMnO_4$, laboratory grade – purity 99%.
8- Sulfuric acid H_2SO_4, laboratory grade – concentration 98% and density 1.84gr/cm^3.

Commercial grades were used in pulping and bleaching processes to simulate the industrial conditions, while high-quality laboratory grades were used in the study of bleaching kinetics to maintain accuracy in titrations as hydrogen peroxide is sensitive to metallic impurities. The waste paper pulp composition was maintained in all experiments as the following: 50% old corrugated carton, 30% newsprint and 20% Kraft paper.

This specific composition was chosen in particular to simulate, as possible, the make-up of waste paper mixture in Syrian community, in order to make research outcomes more realistic and applicable. The paper grades used in this research were free of any type of ink, so that applying a deinking stage is not needed. Pulp consistency was maintained at 8%, which we consider as an average value. In that, OCC is pulped typically at 4-5% consistency, while newsprint is pulped at 10-12% consistency (5).

The devices used in this research are:

1) Laboratory pulper and accessories (the overall system is shown in app. 1)

To conduct research experiments, a special laboratory high consistency pulper was designed for this purpose depending basically on the specifications of corresponding industrial pulpers. After applying the needed reductions in dimensions, certain modifications have been inserted to the laboratory pulper design to give it special features necessary to match research goals. Given that, those modifications has not affected or changed the hydrodynamic features. For example, the mixing and pulping pattern presented in industrial pulpers is exactly introduced in this pulper. Hereafter, a description of the designed system:

1-1 Laboratory pulper

It consists of the two following primary sections, figure 1:

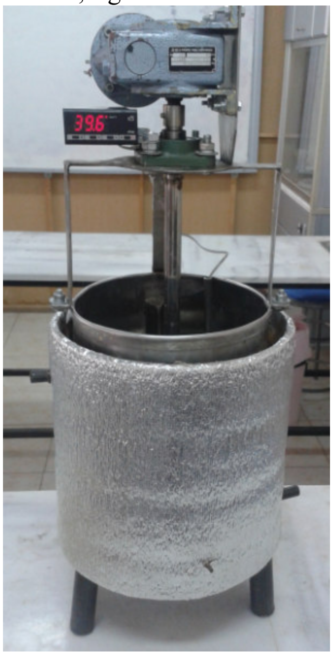


Figure 1: The laboratory pulper

1-1-1 Reactor vessel

It is inside where the whole treatment processes take place (Figure 2), and it comprises the following parts:

Figure 2: Reactor vessel

Internal vessel made of iron-chrome alloy which endures reaction conditions. Inside this vessel, pulping and bleaching reactions occur. It is equipped with a small side opening for sampling (3 mm diameter) with manual valve, and a bottom drain manual valve, figure 3.

On the inner wall of this vessel, there are three baffles made of the same alloy and distributed uniformly on the inner wall. Their purpose is to improve mixing and pulping inside the reactor by redirecting the viscous pulp flowing near the inner wall towards the rotor.

In addition, a small iron-chrome tube designated for the temperature sensor is fixed on the inner wall. With its open top and bending bottom toward vessel center, the tube will allow the sensor inside to accurately measure pulp temperature while being minimally influenced by the inner wall temperature, figure 4.

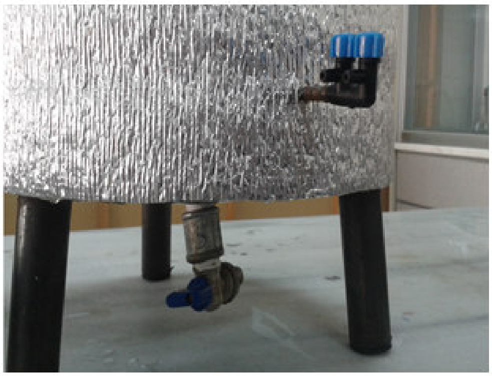


Figure 3: Sampling & drain openings and base legs

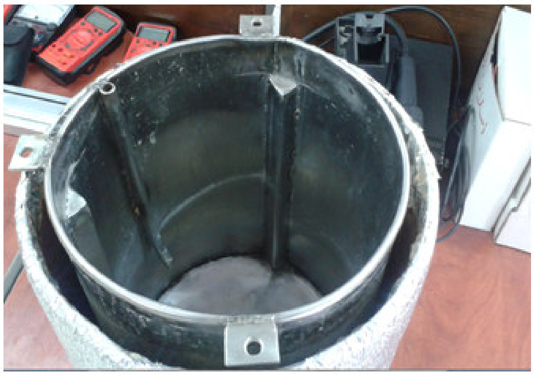


Figure 4: Interior baffles and temp. sensor tube

- External vessel made of iron and surrounds the internal one, forming a heating jacket in which hot water flows to heat the internal vessel and maintain the desired temperatures. The hot water enters the jacket through an upper opening coming from water heating basin and goes out from a lower opening on the opposite side to be poured again in the same basin, heated and repumped again, completing the hot water cycle (heating jacket inlet and outlet are shown in figure 1). The External vessel is covered with an insulator to minimize thermal loss.

- Convex base made of iron – chrome alloy, with three attached legs made of Iron equipped with rubber endings to reduce vibration, figure 3.

1-1-2 <u>Mixing system</u>

This system, figure 5, aims to provide mixing inside the reactor vessel as being fixed on its top. The system consists of the following parts:

Figure 5: Mixing system

- **Motor base**

It is a metallic base made of iron – chrome alloy and has three fixation arms distributed uniformly on about 60% of the perimeter of internal vessel top. That is to keep a space for chemicals additions, monitoring the process and cleaning the pulper afterwards. Motor bearing is fixed on this base, attached with a special slot for digital temperature controller, figure 6.

Figure 6: Electrical motor base

- **Electrical motor**

For mixing and pulping purposes, the device is equipped with 24 V - DC motor with gearbox. It is capable of providing the required power for research processes with rotation speed up to 300 rpm, figure 6.

- **Rotation axis and rotor**

These two parts are also made of iron – chrome alloy. The axis can be adjusted up and down to obtain a proper height (figure 5), and it is connected with a conical rotor structured according to the industrial rotor design (figure 7). The ratio of rotor to reactor diameters is modified and managed to maintain the same hydrodynamic features after transferring from industrial to laboratory scale.

Figure 7: Conical rotor

This rotor is 20 cm height. On its outer surface, two spirals are fixed which start from the top of the rotor and end at 3 cm height from the bottom. When the rotor rotates clockwise, the pulp between the spirals will be forced to move downwards to the bottom of the rotor pressured by the spirals' blades. At the bottom part, four small bended blades are fixed and distributed uniformly on rotor base. They aim to exert centrifugal forces on the pulp descending from the spiral section and push it, therefore, to the inner wall of the internal vessel. Because of continuous rotation and centrifuging the pulp, the latter goes up in the zone near the wall until it reaches the surface. There, due to gravity and internal baffles, the pulp is directed to the center of the pulper, where the spirals push it downwards again and the cycle is repeated, figure 8. Thereby, the mixing, pulping and bleaching take place.

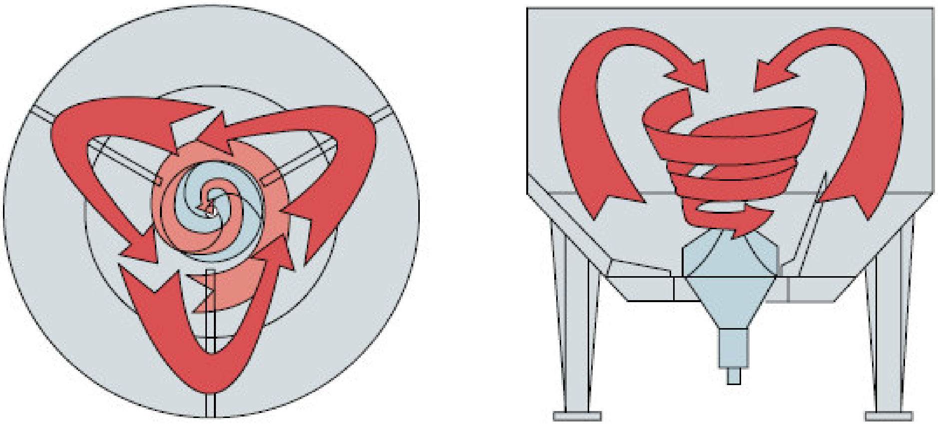


Figure 8: The pattern of pulp flow inside the reactor.

1-2 Laboratory pulper accessories

- 24 V transformer which supplies the electrical motor with 24 V DC. It is equipped with a special switch to adjust the rotation speed of the motor.
- Separated water heating basin to heat the water pumped to the jacket.
- Small submersed pump to transfer the hot water from the basin to the heating jacket.
- Digital temperature controller connected to the temperature sensor that measures pulp temperature inside the reactor. According to the difference between the measured temperature and the given set point, the controller will cut off or supply the electrical current to the hot water pump.

- Plastic and metallic valves and tubes to complete hot water circuit.

2) HVI device

This device is used to measure the final brightness of the pulp after each experiment, figure 9. Its principle is to measure (on a scale from 0 to 100%) the percentage of the reflected light waves upon the surface of the sample prepared from the treated pulp after each experiment. The end 100% of the scale refers to the light reflection from magnesium oxide surface.

Figure 9: HVI device.

3. Experiments methodology

Five experiments were conducted with different bleaching times as shown in the following table:

Table 1: Bleaching process time in each experiment

Experiment	**First**	**Second**	**Third**	**Fourth**	**Fifth**
Time (min)	50	60	70	80	90

The other conditions of bleaching process were maintained at the following values:

Table 2: The constant values of bleaching process variables

Consistency	**H_2O_2 con.**	**NaOH con.**	**Na_2SiO_3 con.**	**Temperature**	**Rotation speed**
8%	2%	0.1%	1.5%	50°C	300 rpm

The concentrations of H_2O_2, NaOH and Na_2SiO_3 are based on dry pulp mass.

4. Experimental procedure

Here are the steps followed for each experiment:

- Based on 8% consistency and using four liters of water, the required solid mass of paper for each experiment is calculated from the following equation:

Consistency = (Solid mass) / (Solid mass + Water mass)

The four-liter quantity of water is chosen for its appropriateness for the pulper volume. The calculated solid mass (dry pulp mass) is then divided between paper grades according to the percentages mentioned above (Section IV).

- After adding the previous volume of water to the pulper, conditions within are adjusted to meet pulping ones, namely 50°C and pH = 10 (2).
- The pulping stage starts once waste paper is added to the pulper, after being shredded to small and medium pieces to ensure smooth pulping process.
- Pulping stage lasts for 20 minutes, as then the pulp is formed. Right after, the bleaching stage begins.
- Bleaching chemicals are added to the pulper according to the values mentioned in table 2.
- Since the beginning of the bleaching stage and at equal consecutive intervals of 10 minutes, two samples are taken periodically, where each sample is 10 ml, to study the kinetics of the bleaching reaction between H_2O_2 and chromophores. Each sample is acidified with sulfuric acid 2N and titrated with potassium permanganate $KMnO_4$ 0.05N until color changes. Using the consumed volume of $KMnO_4$, H_2O_2 concentration in the titrated sample can be calculated, and a curve of the decreasing concentration of H_2O_2 with bleaching time can be drawn.
- Bleaching stage lasts for the predetermined time for each of the five experiments.
- As bleaching stage ends, a proper amount of pulp is taken out the pulper, and washed with fresh water for 5 minutes to remove bleaching liquor and neutralize pulp pH to avoid alkaline yellowing reactions.
- The washed pulp is then flattened and left for enough period to dry in laboratory atmosphere.
- The dried pulp is cut into three similar parts whose dimensions are suitable with those of the slot of brightness measuring device. Those parts are the samples whose brightness is measured.

- The brightness is measured by placing the sample in the dedicated place (slot) in HVI device, with the top surface opposite to the light. The process is repeated to determine the brightness of all three samples then an average value is reckoned.
- After finishing the experiment, the pulper is dismantled, cleaned and then reassembled for the next experiment.

5. Results and discussion

After measuring the brightness of all samples, the following results were obtained:

Table 3: Brightness values at different bleaching times.

Experiment	First	Second	Third	Fourth	Fifth
Time (min)	50	60	70	80	90
Brightness (%)	50.02	50.93	51.17	51.26	51.33

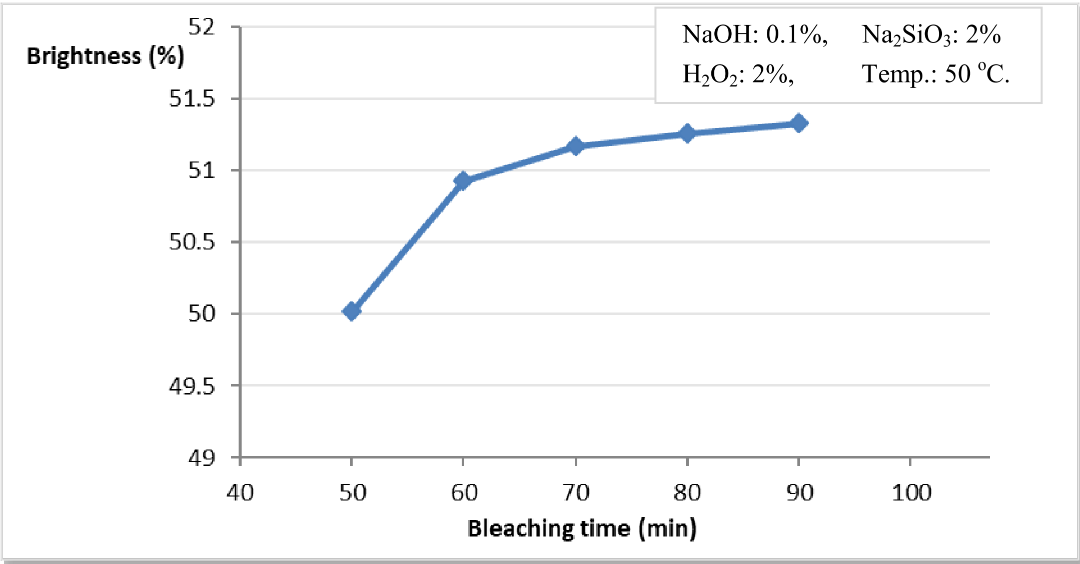


Figure 10: Brightness level versus bleaching time at conditions shown in table 2, with pulp composition: 50% old corrugated carton, 30% news print and 20% Kraft paper.

The previous figure shows that brightness increases with bleaching time. This seems reasonable as extending the process time will allow the bleaching reaction to remove more chromophores, giving consequently higher brightness. But, on the other hand, it is noticed from figure 10 that the increment in brightness decreases gradually as the duration of bleaching process extends within the studied range. This could be ascribed to the continuous reduction in the number of the remaining removable chromophores as the bleaching process proceeds, which makes this process less effective at the end of relatively longer treatment times. Another possible underlying factor is that the rate of bleaching reaction lowers over time due to the progressive decrease in hydrogen peroxide concentration in the reactor. As a result of the previous two reasons, the positive impact of increasing bleaching time on brightness diminishes gradually.

It can also be shown that the gain in brightness at process times longer than 70 min is comparatively insignificant. Such thing could make any extension in process time above this value unjustified in view of the associated higher energy consumption and lower yield when talking about industrial applications. Accordingly, it could be said that the optimum bleaching process time as per to research conditions is 70 min. In that, the most brightness gain would be achieved at this time. This optimum value could differ drastically when other conditions change.

Those foresaid results are in line with the ones of (11) and (9), which conclude that the major increase in brightness occur in the first 60 min of the bleaching process. However, the previous figure demonstrates that lessening bleaching time process below 60 min without any change in other conditions may reduce process efficiency and result in remarkably lower brightness levels.

- **Kinetics of Bleaching reaction**

By analyzing samples which were taken at equal intervals of 10 minutes starting from the beginning of bleaching stage, the following curves were obtained:

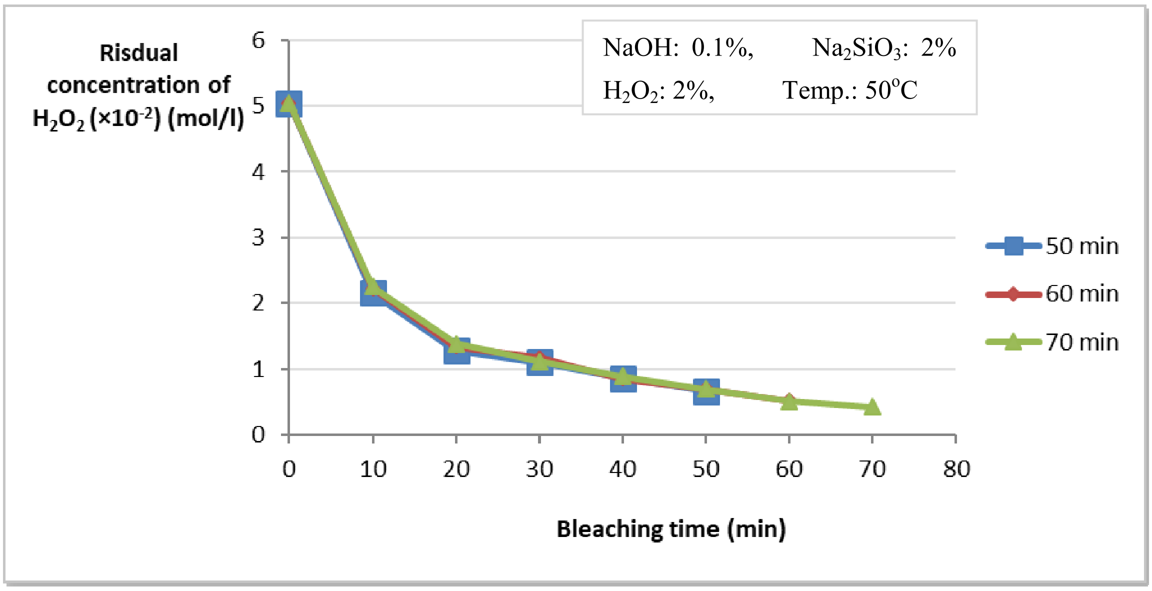


Figure (11, a): Bleaching reaction kinetics at three different times of bleaching process (50, 60 and 70) min at conditions shown in table 2 with pulp composition: 50% old corrugated carton, 30% news print and 20% Kraft paper.

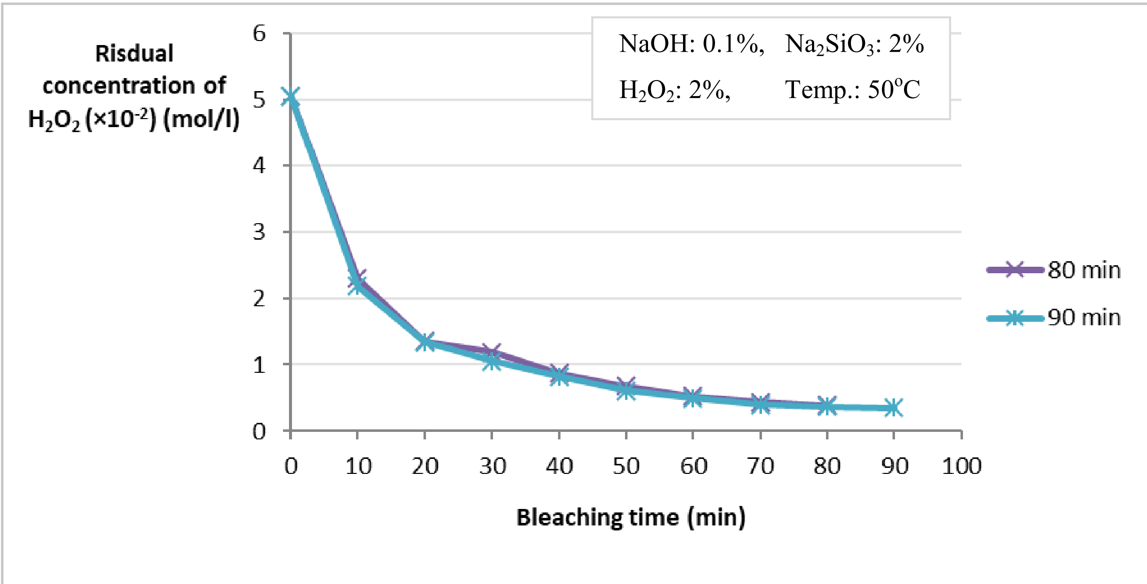


Figure (11, b): Bleaching reaction kinetics at two different times of bleaching process (80 and 90) min at conditions shown in table 2 with pulp composition: 50% old corrugated carton, 30% news print and 20% Kraft paper.

The figure (11, a) show that applying relatively short bleaching times will result in high residual of H2O2 at the end of the treatment. For example, the final concentration of the peroxide when applying bleaching time of 50 min is 0.67×10-2mol/l comparing with 0.42×10-2mol/l at the end of the 70-min experiment. Because the difference in final brightness between these two experiments is obviously significant, a change in one or more of other bleaching process variables should be done when applying short bleaching times to avoid lower brightness, higher peroxide residual and, therefore, less efficiency. Such changes could be a higher initial NaOH concentration or higher operating temperature as found in similar other studies.

6. Conclusions

1- The brightness of the de-inked waste paper pulp rises as bleaching time increases over the whole studied range.
2- A 70 min bleaching time was argued to be optimum. In that, extending process duration more than this will give only slight brightness gain, which would be unwarranted in view of the associated higher energy usage and lower yield on the industrial scale.

3- Reducing process time below 60 min will cause comparatively lower brightness and efficiency, unless certain modifications in other variables are applied.

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