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A Study of the Influence of Temperature on Bleaching Process of the De-Inked Waste Paper Pulp using Hydrogen Peroxide

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Abstract
This research aims to study temperature influence on the bleaching process 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 studied temperatures. This research also studies the kinetics of the bleaching reaction at each studied temperature.The experiments were conducted using a laboratory pulper designed to simulate the industrial pulpers, but also modified to meet goals and conditions of the research.The results show that brightness increases as temperature increases, and an optimum temperature for bleaching process at research conditions was determined. The results also show that lower temperatures of the studied range result in relatively low brightness levels, while higher temperatures increase thermal decomposition of hydrogen peroxide, what effects negatively on bleaching process efficiency.
Keywords: Bleaching, Temperature, Brightness, Hydrogen peroxide

I- Introduction

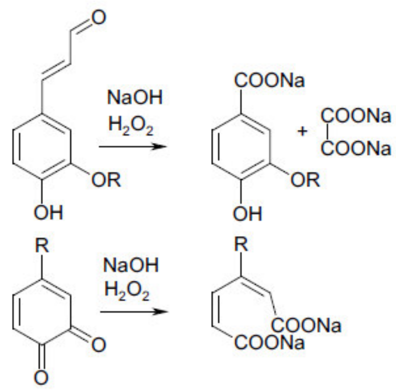
As attention toward recycled fibers has recently increased for ecological and economical reasons, it was necessary to find new ways to improve recycled pulp properties to make them meet the high requirements in paper market. In spite of the application of several processes to remove contaminants from waste paper, producing high quality products required additional process to achieve high optical properties of paper. This process is bleaching (Bajpai, 2014) (Renders, 1995).

II- 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 (Sixta, 2006a). The color is due to the presence of unsaturated chemical structures called chromophores (Sixta, Potthast, & Krotschek, 2006b), which most of them are existed in lignin compounds. Lignin is a substance comes from wood, the origin of most paper grades, as an amount of it, depends on the produced paper grade, still exists in paper after processing wood in integrated paper mills (Roberts, 1996). The chromophores give the pulp a dark color, through absorbing a portion of the light spectrum by means of the conjugated bonds system existed in these structures, and a very small amount of chromophores are enough to give the pulp a darker color. Bleaching process alternates the chemical composition of these chromophores, giving in result a brighter pulp (Stenesh, 1989) (Sixta, Potthast, & Krotschek, 2006b).

There are many chemical agents that are applied to achieve bleaching, some of them are oxidative while the others are reductive (Borchardt, 1995). Among these various compounds, hydrogen peroxide H_2O_2 is considered as the most favorable chemical for bleaching waste paper pulp, due to its effectiveness in increasing pulp brightness and its correspondence with environmental requirements (Werner, 2006) (Renders, 1995). Therefore, we used this chemical as a bleaching agent in this research.

In alkaline conditions, hydrogen peroxide reacts with chromophores and alters their composition to colorless forms, as shown in the following equations (Süss, 2010):



Bleaching can be performed in one point or more along the process line of waste paper, but due to the reduction in brightness caused by alkaline conditions in the pulper, hydrogen peroxide is usually added to it to compensate this reduction (Bajpai, 2014). Stabilizing agents, like sodium silicate, are also added to stabilize hydrogen peroxide. Those agents remove metallic ions that reduce hydrogen peroxide stability and catalyze its decomposition (Borchardt, 1995).

In alkaline conditions, bleaching process using hydrogen peroxide is activated by producing perhydroxyl anion HO_2^-, as shown in the following equation (Bajpai, 2012):

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

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

III- Research objective:

This research aims to study the influence of temperature on the hydrogen peroxide bleaching process of deinked waste paper pulp, through investigating how pulp brightness changes with process temperature while maintaining other variables constant. The research also studies the kinetics of bleaching reaction between hydrogen peroxide and chromophores, through monitoring how hydrogen peroxide concentration decreases with process time at each applied temperature.

IV- Materials and devices:

- These 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 1.525 gr/cm^3 and SiO_2: Na_2O ratio is 2:1.
6- Hydrogen peroxide solution H_2O_2, commercial grade – concentration 35.8% and density 1.16 gr/cm^3.
7- Potassium Permanganate $KMnO_4$, laboratory grade – purity 99%.
8- Sulfuric acid H_2SO_4, laboratory grade – concentration 98% and density 1.84 g/cm^3.

Commercial grades were used in pulping and bleaching processes to simulate the industrial state, while laboratory grades were used in studying of bleaching reaction kinetics, to maintain accuracy in titrations as hydrogen peroxide is sensitive to metallic ions existence.

The waste paper pulp composition was maintained in all experiments as the following:

- 50% Old corrugated carton.
- 30% News print.
- 20% Kraft paper.

This composition was chosen to simulate the composition of waste paper mixture in Syrian community as possible, which makes the results of this research more beneficial on the practical side. The paper grades used in this research are free of any type of ink, to compensate applying a deinking stage.

Pulp consistency was maintained at 8%, which is an average value, as OCC is pulped typically at 4-5% consistency, while newsprint is pulped at 10-12% consistency (Roberts, 1996).

- The devices used in this research are:

1) Laboratory pulper and accessories (appendix 1):

To conduct research experiments, a special laboratory high consistency pulper was designed for this purpose, depending basically on specifications of industrial pulpers. Certain modifications has been inserted to its design due to the required reductions in dimensions, according to local possibilities and to give the designed pulper some special features that help achieving research goals, given that, these modifications has not affected or changed the mixing and pulping pattern applied in industrial pulpers. Here is a description of the designed pulper:

- Laboratory pulper:

The pulper (Figure 1) consists of two primary sections:

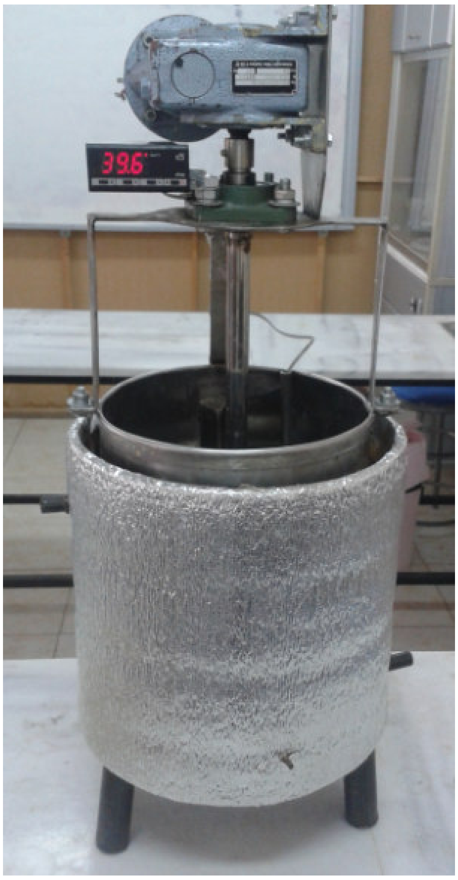


Figure 1: The laboratory pulper

1- <u>Reactor vessel:</u>

It is where the pulping and bleaching reaction takes place (Figure 2), this reactor consists of the following parts:


Figure 2: Reactor vessel

- Internal vessel made of Iron-Chrome alloy which resists reaction conditions. Inside this vessel pulping and bleaching processes take place. It has a small side sampling opening (3 mm diameter) with manual valve, and a bottom drain opening with 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 by redirecting the pulp existed near the inner wall towards the rotor.

The internal vessel has also a small tube for temperature sensor, it is opened form the top and bended at the bottom toward vessel axis, to measure pulp temperature accurately, with least influence of inner wall temperature, Figure 4.

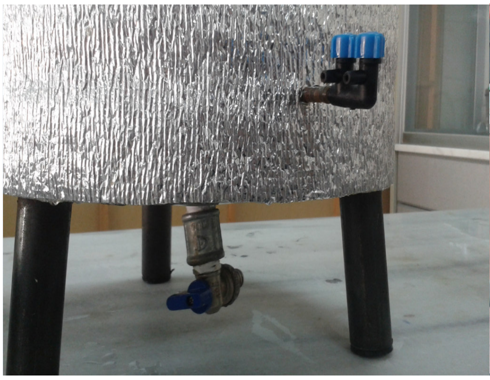


Figure 3: Sampling and Drain openings

Figure 4: Interior baffles and temp. sensor tube

- External vessel made of iron and surrounds the internal one forming a heating jacket, which used to heat the internal vessel to the required temperature by means of hot water. Hot water enters the jacket through an upper opening coming from water heating basin and goes out through a lower opening on the opposite side (hot water inlet and outlet are shown in figure 1). The External vessel is covered with insulator to minimize thermal loss.
- Convex base made of iron – chrome alloy, with three legs made of Iron equipped with rubber endings to reduce vibration.

2- Mixing system:

This system (Figure 5)consists of the following parts:

Figure 5: Mixing system

- Motor base:

It is a metallic base made of iron – chrome alloy, and has three legs for fixation, and distributed uniformly on just 60% of perimeter of internal vessel top, and that is to keep a space for chemicals additions, monitoring the process and cleaning the pulper. Motor bearing is fixed on this base which is also 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, capable of providing the required power for research processes, with rotation speed of 5 turn/sec, 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 maintain a proper height (figure 5), and it is connected with a conical rotor that is designed according to the industrial one, figure 7.

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, where four small bended blades are existed and distributed uniformly on rotor base. Those blades exert centrifugal forces on the pulp, therefore, push it to the inner wall of the internal vessel. Due to continuous rotation, the centrifuged pulp goes up to the surface nearby the wall, where it is directed again by gravity and internal baffles to the center of the pulper, where the rotor pushes it downwards, and the cycle is repeated again. By this way, pulping and bleaching take place.

- Laboratory pulper accessories:
  - 24 V transformer that supplies the electrical motor with the required electrical energy. It is equipped with a special switch to control the speed of the motor.
  - Separated water heating basin to heat the water which is pumped to the heating jacket.
  - Small submersed pump, to transfer the hot water to the heating jacket.
  - Digital temperature controller, with sensor to measure the temperature of the pulp inside the reactor. According to the difference between the measured temperature and the given set point, the controller will cut off or supply the water pump with electrical current.
  - Plastic and metallic valves and tubes to complete heating water circuit.

Figure 8: HVI device.

2) HVI device:

This device is used to measure the brightness of the pulp after each experiment, it has the principle of measuring the percentage of the reflected light waves from the surface of the sample, which is taken from the pulp after each experiment. The end 100% of the scale refers to the light reflection from magnesium oxide surface, Figure 8.

V- Experiments methodology:

Five experiments were conducted at different temperatures as shown in the following table:

Table 1: Values of temperature in each experiment

Experiment	First	Second	Third	Fourth	Fifth
Temperature °C	30	40	50	60	66

Other bleaching conditions were maintained at the following values:

Table 2: Constant values of the other variables

Consistency	H_2O_2 concen.	NaOH con.	Na_2SiO_3 con.	Bleaching time
8%	2%	0.1%	1.5%	60 min

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

VI- Experimental procedure:

Here are the steps followed for each experiment:

- We calculate the required solid mass of paper for 8% consistency and 4 liter of water, as it is enough and suitable volume of water according to pulper volume, from the following equation:

$$\text{Consistency} = (\text{Solid mass}) / (\text{Solid mass} + \text{Water mass})$$

The obtained solid mass (dry pulp mass) is then divided between paper grades according to percentages mentioned above.

- After adding the previous volume of water, conditions in the pulper are adjusted to meet pulping ones which are 50°C and pH = 10 (Renders, 1995).
- The pulping stage starts as 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, and then 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 intervals of 10 minutes, we take two sample periodically, each sample is 10 ml, to study the kinetics of 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. Through the consumed volume of $KMnO_4$, H_2O_2 concentration in the titrated sample can be calculated, and a curve of H_2O_2 concentration decreasing with bleaching time can be drawn.
- Bleaching stage lasts for 60 minutes.
- 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 to neutralize pulp pH to avoid alkaline yellowing reactions.
- The washed pulp is then flattened and left for enough period to be draught in laboratory atmosphere.
- The dried pulp is cut into three parts with dimensions suitable with brightness measuring device. Those three parts are the samples whose brightness is measured.
- Sample brightness is measured by placing the sample in the dedicated place in HVI device, with the top surface is opposite to the light. The brightness of the three samples is measured and an average value is calculated.
- After finishing the experiment, the pulper is dismantled, cleaned and then reassembled for the next experiment.

VII- Results and discussion:

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

Table 3: Brightness values at different temperatures

Experiment	First	Second	Third	Fourth	Fifth
Temperature (°C)	30	40	50	60	66
Brightness (%)	49.1	50.1	50.93	51.63	51.7

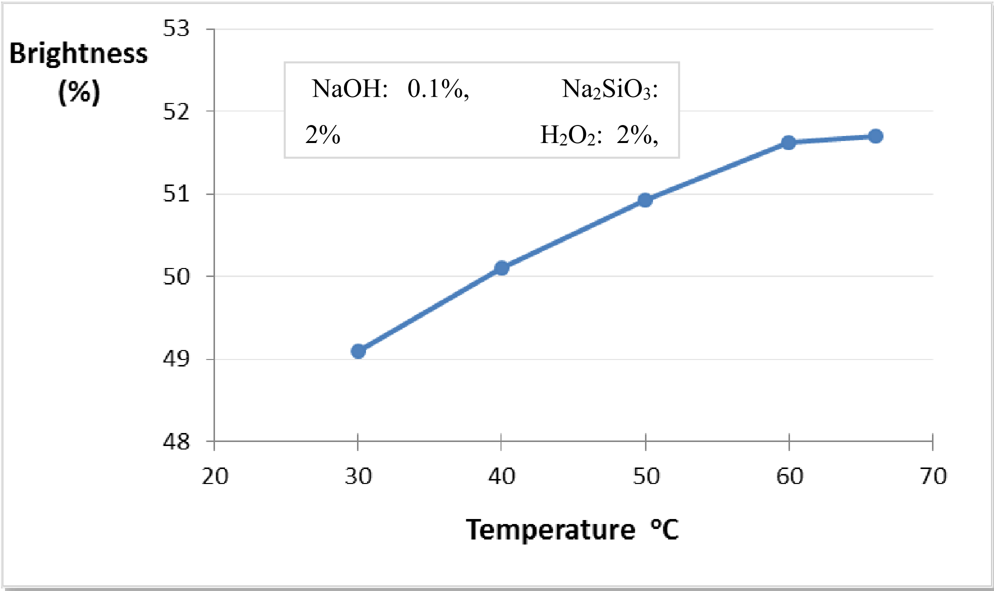


Figure 9: Brightness changes versus temperature at research conditions.

The previous figure shows that brightness increases as temperature increases, this could be explained in that temperature increases bleaching reaction rate, and that leads to higher consumption of hydrogen peroxide in bleaching process instead of being consumed in undesired reactions like decomposition due to alkaline conditions or heat, what gives in turn higher brightness levels. But when it comes to temperatures more than 60ºC, the gain in brightness was too small and that could be a result of thermal decomposition of H_2O_2, which becomes faster as temperature increases, and a state of balance may have occurred between bleaching and decomposition reactions, that lead to a very small gain in brightness after 60ºC. The thermal decomposition of H_2O_2 occurs according to the following equation:

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2$$

This means that applying higher temperatures in bleaching waste paper pulp according to this research conditions may not be justified, considering both, the energy required to raise bleaching process temperature and the low gain in brightness above 60ºC that did not exceed 0.1%. That means 60ºC is the optimum temperature to apply bleaching process as per to research conditions.

The figure 9 also shows that applying low temperatures in bleaching process reduces process efficiency and lead to relatively low levels of brightness.

- Kinetics of Bleaching reaction:

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

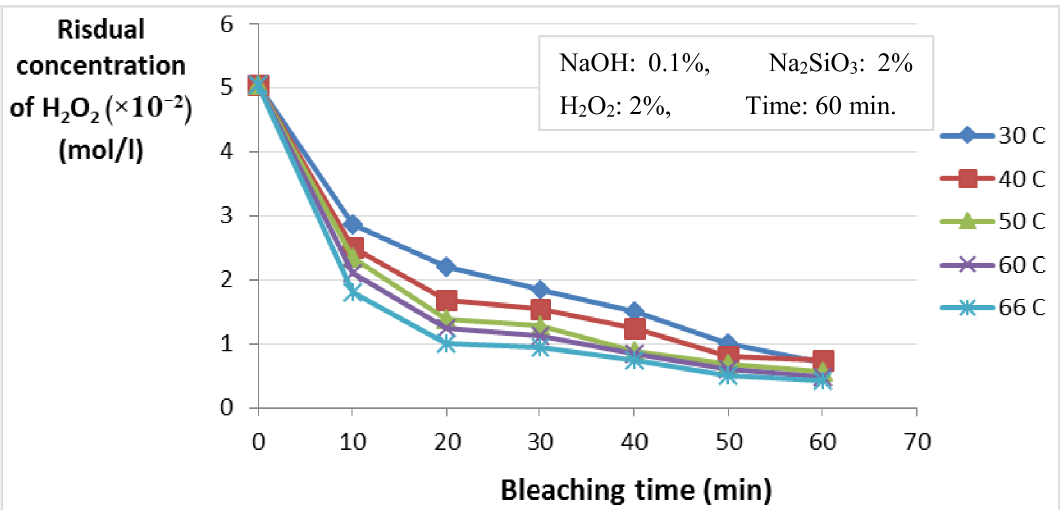


Figure 10: Bleaching reaction kinetics at different temperatures.

The figure shows how H_2O_2 concentration decreases with time, it also shows that the higher the bleaching temperature, the higher H_2O_2 consumption, and this interprets the higher levels of brightness gained at elevated temperatures, but on the other hand, the higher consumption of peroxide does not always mean that it is consumed in bleaching, just like the case above 60ºC.

VIII- Conclusions:

1- The brightness of de-inked waste paper pulp increases with bleaching process temperature, and it was shown that 60ºC is the optimum bleaching temperature as per to research conditions.

2- Low bleaching temperatures may lead to low levels of brightness and decrease process efficiency.

3- Attention should be paid when applying high bleaching temperature, as thermal decomposition of H_2O_2 becomes faster.

A further study of extended temperature range may give us a better look of how pulp brightness changes above the studied range of this research.

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X- Appendix 1: Work system (laboratory pulper and accessories) from two perspectives**:**