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# Temperature effect on an ultrasound-assisted paper de-inking process

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ABSTRACT

The influence of temperature on an ultrasound-assisted ink removal process has been investigated. White copy paper was evenly soaked in black writing ink. After drying the paper to constant weight at 75 °C, ink removal was attempted under varying conditions. Results were assessed by monitoring the UV–vis absorbance of the aqueous phase and measuring the brightness of the paper. Sonication was observed to improve the brightness of the paper in the temperature range of 15–45 °C with an optimum effect at 35 °C. Monitoring UV–vis spectra of the aqueous phase provided evidence that modification of the chemical structure of the ink desorbed from the paper occured. Further investigation under the same conditions showed that ink, when not absorbed on paper, did not undergo the same chemical change. This supports the hypothesis that only the compound released from the ink absorbed onto the paper is sensitive to sonodegradation. One possible explanation is that the metal binding component of the ink stays absorbed on the paper, releasing the organic part, whose chemical structure can be altered by the effect of sonication. Inductively coupled plasma analysis was used to confirm that during the de-inking process of the paper, the metal binding component stays absorbed on the paper and only the organic part is released in the aqueous phase.

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## 1. Introduction

In recent years, interest in paper recycling has increased for a number of environmental reasons. A major problem associated with paper recycling is the whitening process, with emphasis being placed on the production of brighter de-inked pulps. Traditionally, oxidizing agents are used to improve the de-inking process and whitening of the paper pulp. Among them are hydrogen peroxide [1], ozone, chlorine dioxide, hypochlorite, dithionite and formamidine sulfinic acid [2]. Ultrasound has been utilized in the paper processing industry at different stages; of which enhancement of pulping, bleaching, depolymerisation of cellulose and treatment of wastepaper have been reported [3–6]. During the process of bleaching, ultrasound has been used to enhance the de-inking of recovered paper when traditional alkaline treatments were not satisfactory [7–12]. These studies report the successful use of ultrasound with temperatures up to 90 °C, in some cases in the presence of additives. In addition, ultrasound has been shown to improve the quality of paper fibers recovered in the recycling process [13]. Other studies report that when varnish is present, optimum results have been attained at temperatures of 65 °C [14]; 70 °C [15] or 80 °C [8], as heat is needed to soften the varnish present. However, excluding one paper that discusses the influence of temperature (20 °C, 40 °C and 60 °C) on the removal of indigo dye from paper in the presence of ultrasound [6], no previous study has investigated the effect of sonication at lower temperatures on unvarnished paper. Furthermore, the articles cited above describe the influence of ultrasounds on the ink particle size but not on its chemical structure.

The main advantage of using sonication resides in the fact that experiments can be carried out at close to ambient temperature under atmospheric pressure contrary to other advanced oxidation processes. The propagation of the acoustic waves in a liquid produces the phenomenon of cavitation [16]. The non-linear expansion and sudden collapse of microcavities result in tiny areas of very high temperature (up to 5000 K) and high pressure (500–1000 atm) [17]. Under these highly localized but harsh conditions, formation of radicals may occur [18,19]. For instance, sonolysis of water generates hydroxyl radicals and hydrogen atoms [20]. These particles may recombine to form hydrogen and hydrogen peroxide or may react with the species present in the solution. Moreover, the high temperature and pressure conditions may contribute to the pyrolysis of volatile and hydrophilic chemical species.

The effectiveness of ultrasound-assisted processes is often affected by temperature [21]. With an increasing temperature of the solvent, dissolved gases and solvent vapors enter the cavitation bubbles. This reduces the collapse and the effectiveness of the cavitation process. However, cavitation may be reduced when working at lower temperatures, since a more viscous medium hinders

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acoustic wave propagation. Given such an influence the effect of temperature on the de-inking process of unvarnished inked paper has been investigated.

## 2. Experimental set up

### 2.1. Materials

The 20 kHz sonication probe with a 750 W output, was manufactured by Sonics and Materials. A Suslick reaction vessel from Sonics (250 ml, three necks, flat bottom glass sonoreactor with a chamber height of 162 mm) was used. The amplitude was set at 70%. A 9 s on and 9 s off duty cycle was used for the experiments. The experiments were carried out in a temperature control water bath from Forma Scientific (model 2067). Xerox acid free paper (Business 4200) and Waterman black writing ink were used. Analytical grade nitric acid 15.8 M $HNO_3$ from Acros Organics was used and diluted with deionized water to 7.9 M $HNO_3$ as needed. Anhydrous ethanol was purchased from Fisher Scientific. Whatman silica gel TLC plates were used. A UVG11 UV lamp (254 nm) from UVP Company was used for TLC analysis.

Ultraviolet–visible spectra were recorded using a Varian Carey IE spectrophotometer. The brightness of the paper residues was measured with a Technidyne Brightimeter S-5, with a 45° illumination and reading at 0°. The orifice was taped such that a 3 × 2 mm area was illuminated, providing a relative input allowing for a comparison within the samples. Except for the brightness measurements, each experiment was duplicated under identical conditions, thus the data are expressed as the mean value with the standard deviation. Photographs were taken with a Canon 20D camera, with an exposure of 1/160 s at f/11 and a lens focal length of 50 mm.

The inductively coupled plasma (ICP) data was collected on a Perkin–Elmer Plasma 4000 emission spectrometer. The $1.0 \times 10^3$ ppm metal standards for the ICP analysis were purchased from SPEX CertiPrep Group.

### 2.2. Ultrasonic power measurement

Due to heat loss, the actual acoustic power dissipated in solution, $P_{diss}$, is lower than the maximum irradiated power, $P_{max}$ [22]. In order to compare data and ensure reproducibility, $P_{diss}$ has to be calculated. Calorimetry allows the calculation of $P_{diss}$, [23,24], with the assumption that all power entering the reaction solution is dissipated as heat, using the following equation:

$$P_{diss} = (dT/dt)_{t=0} \cdot m_{water} \cdot C_{water} \quad (1)$$

where $m_{water}$ is the mass of the water, $C_{water}$ the heat capacity of the water and $(dT/dt)_{t=0}$ the change of temperature with respect with time. The value for $(dT/dt)_{t=0}$ is calculated from the initial slope of the increase of temperature of the water as a function of time when sonicated without any temperature control. Ultrasonic power measurement data were obtained when 100.0 ml of deionized water at 35 °C was sonicated without any temperature control. The temperature change, $dT/dt$, was recorded every nine seconds for eight minutes and then every four minutes for a total time of twenty five minutes. After thirteen minutes of sonication, the temperature reached a plateau at 81.9 ± 0.1 °C. The results are plotted in Fig. 1. Under these conditions, $P_{diss}$ was calculated for the first 27 s to be 83.7 ± 0.1 Watts.

### 2.3. Paper inking

Two centimeter-edge squares of white paper were dried to constant weight overnight in a 75 °C oven. The paper was then soaked evenly in ink for 15 min, dried to constant weight overnight in a 75 °C oven and weighed. The average ink loading was $(4.7 \pm 0.1) \times 10^{-4}$ g/cm$^2$. The paper squares were stored in an air tight plastic bag in a refrigerator.

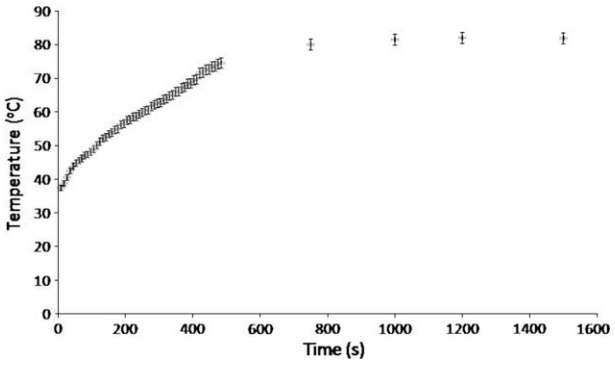


**Fig. 1.** Ultrasonic power measurement: Temperature increase as a function of time.

### 2.4. Sonodegradation of inked paper

The sonoreactor containing 100.0 ml of deionized water was placed in a temperature regulated water bath (15–45 °C). When the water in the sonoreactor reached the desired temperature, two squares of inked paper were added. The sonoreactor was then covered with aluminum foil to avoid any interaction between light and the samples. Sonication was immediately started for the required amount of time (5–30 min). At the end of the experiment, the reaction mixture was filtered, diluted by a factor of 10 with deionized water and the filtrate was analyzed by UV–vis spectroscopy. The paper residue was dried at room temperature overnight, photographed and the brightness was measured.

### 2.5. Ink sonodegradation

In the sonoreactor, 4.0 mg of ink was diluted into 100.0 ml of deionized water. This solution was sonicated for 60 min at 35 °C. Sampling was performed every minute for the first 5 min, then every 5 min for the next 25 min and at the 60 min mark. Samples were filtered, diluted by a factor of 10 with deionized water and the solution was analyzed by UV–vis spectroscopy.

### 2.6. Sonodegradation of the aqueous solution of desorbed ink

Two squares of inked paper were stirred at 35 °C for 30 min in 100.0 ml of deionized water. After removal of the paper by filtration, the filtrate was sonicated at 35 °C for 60 min. Samples were diluted with deionized water by a factor of 10. Monitoring by UV–vis spectroscopy was performed every 5 min in 6 consecutive intervals (30 min total) and then at the 60 min mark.

### 2.7. Thin layer chromatography

A solution consisting of 4.0 mg of ink diluted in 100.0 ml of deionized water, the filtrate obtained in part 2.6 before sonication and after sonication, were spotted on a TLC plate. The TLC plate was eluted with ethanol and analyzed at 254 nm with a UV lamp.

### 2.8. Iron, manganese and copper analysis by ICP spectrophotometry

#### 2.8.1. Metal identification

The most likely binding metal components in the ink samples are iron, manganese and copper [25,26]. Commercially available standardized aqueous solutions of iron, manganese and copper