The Production and Optimization of Printing Ink Derived from Waste Tire Carbon Black

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DOI: https://doi.org/10.51244/IJRSI.2025.12010039

Received: 13 December 2024; Review: 30 December 2024; Accepted: 04 January 2025; Published: 08 February 2025

ABSTRACT

The use of waste tire carbon black from locally sourced in printing ink production was explored as it poses to be both environmentally friendly and economically viable investment. Carbon black pigment was obtained from the pyrolysis of tire, then it undergoes acid demineralization by dissolving the sample in concentrated hydrochloric acid for the period of 24hrs, the sample was then filtered and rinsed thoroughly with distilled water to eliminate unwanted composite that might affect the pigment from giving it best quality, after that the sample was dried in an electric oven at 110°C for 8hrs, the dried sample was pulverized again. The formulation of offset printing ink from the obtained black pigment was done by dissolving modified starch in water and stir to obtain viscosity, then stearic acid was added as a coupling agent and heated for 30min using magnetic stirrer to form vanish, after which the prepared sample weight 25g and Isopropyl alcohol were added in to the mixture and stirred for 30min using magnetic stirrer to obtain a homogeneous mixture and uniform distribution of the components. The produced ink from carbon black demonstrated good physical properties which include viscosity, opacity, adhesion, eligibility and erasability. The pH was determined to be 5.3 slightly alkaline is less acidic, the viscosity and surface tension was found 57.80 (mN/m) and 38.90 (Pa.s./25° C) to be respectively. The ultimate analysis of the of Waste Tire Carbon Black shows high percent of carbon at 82.92 wt % these shows the waste tires to be rich in carbon materials as while as other elements as O, S and N. The FTIR spectra of the calcinated waste tire powder identified major peaks as C-H, C=O, C-H and OH identified at 3000 cm^{-1}, 1700 cm^{-1} , 1000-1500 cm^{-1}, and 3500-3600 cm^{-1} respectively, the presence of C-H and C=H stretches confirms the high amount of carbon and hydrogen observed from the analysis and confirms its hydrocarbon composition. These properties were optimized in this study by varying the concentrations different the solvent ratios. It is hoped that this work introduces an economically viable means for the production of erasable ink from local sources as well as contribute to sustainable waste management.

Keywords: Carbon Black, Waste Materials, Erasable, Calcinated, Tire, Ink.

INTRODUCTION

The application of printing inks in our daily life serves as the most important medium of communication, education and decoration in our society. They appear on packaging, textiles, everyday items, print media, catalogs, brochures, and other materials as decorative or informative elements. The four main application procedures are offset, screen printing, gravure, and flexography [1].

Inks are colloidal systems of fine pigment particles coloured or uncoloured dispersed in an aqueous or organic solvent [2]. These are primarily composed of pigments, binders, solvents and additives [3]. One of the relatively new products flooding the Nigeria market today is the crucial educational material called “erasable white board marker” or” temporary marker” used on white board which has now almost replaced the traditional chalk used on black board [2]. This product is in high demand at all level of education. However, all the temporary marker

ISSN No. 2321-2705 | DOI: 10.51244/IJRSI |Volume XII Issue I January 2025

currently in circulation in Nigeria are imported, current techniques employ synthetic materials which drives the costs. This practice drains our economy and hence the drive for finding sustainable methods of producing various components of inks locally. Carbon black (soot) which is the pigment explored in this study is a form of elemental carbon produced by the incomplete combustion or thermal decomposition of hydrocarbons [4]. Carbon black (CB) consists essentially of finely divided that are chemically bonded forming agglomerate chains via weak Van der Waals interactions [5]. CB may have applications in areas [6] and has been produced from different sources such as tyres [7, 8]. About 47% of a tire is rubber, 22% is carbon black (CB), 17% metals, 6% textiles and the rest other additives (ZnO, sulfur, clays and other compounds). Nearly a 74–76% of a tire are are carbon-based materials [9]. The more than 2.5 million tons of scrap tires are disposed every year are becoming a growing environmental problem [10]. Disposal of used tires is a global problem; more than 50% are discarded without any treatment. By the year 2030, the number of waste tires would reach 1.2 billion tires yearly [11]. They constitute one of the most important environmental problems in the world. In the literature, there are many reports on CB synthesis such as: pyrolysis [7, 12], hydrolysis [13, 14], carbonization [12], AC thermal plasma [8] and vapor thermolysis [15]. Commercially available carbon black is produced mainly from furnace black. However, thermal black, lampblack, acetylene black and channel black have all been explored [16, 17]. Primary components to be optimized include pigment, resin and solvent ratios which are raw materials for ink production [18].

The pigment colours in the ink and makes it opaque while resins bind the ink and the surface into a film [19]. The solvents make the ink flow so that it can be transferred to the printing surface. Other additives could also be incorporated to alter the physical properties of the ink if necessary. Arabic gum is natural resin rich in non-viscous soluble fiber [20, 21, 22] widely used industrially as a stabilizer, thickener, emulsifier and to a lesser extent in textiles, ceramics, lithography, cosmetic and pharmaceutical industry. These properties are exploited in this study to optimize the production of inks. Indiscriminate disposal of waste and unused materials which include synthetic and bio-based waste materials on roads, canals and drainages which may be due to poor waste management by the citizen and government need to be curbed. Therefore, this research seeks to produce temporary ink from waste materials such as used tyres. This is hoped will reduce or possible eliminate the importation of temporary ink marker into Nigeria. However, these inks have demonstrated greater stability and flow which are vital for the application of the inks. Ink, also called masi, is a mixture of several chemical components, which has been used in India since at least the 4th century BC. They used fine particles of carbon (lampblack) as the colorant and gum, saps or glues as the vehicles or bonding agents [17]. It is worthy of note to say that this type of markers is made basically for non-porous surfaces such as mirrors, metals, and opaque glass materials. The ink is made from color pigments, chemical solvents and a polymer also called a release agent [20]. Therefore, this research seeks to solve economic and environmental problems which includes; Creation of employment and boosting the nation's economy, reducing health hazard caused by pollution, minimizing the rate of foreign exchange and maker pen importation and waste management.

MATERIALS AND METHODS

Materials: The materials which were employed in this work include; spent automobile tire gotten from motor mechanic workshop in Karu, Nasarawa State.

Apparatus: Electrical furnace, Manual domestic grinder, Sieve, Conical flasks, Electrical weighing balance, Beakers, Electric oven, Scrapper, Thermostat, Magnetic stirrer, pH meter, Digital viscometer

Reagents and Chemicals: All chemicals are (99.5% Analytical grade), Conc. Hydrochloric acid, Distilled water, Modified starch, Stearic acid, Isopropyl Alcohol (IPA), Carbon black pigments from tire.

Sample Preparations

Carbon black: Shredded pieces of spent automobile tire was washed and dried. It was charged into a pre-heated furnace and pyrolytic process commenced at temperatures between (750^{o} C - 900^{o}C) for 110 minutes [23]. A fluffy black residue after the completion of combustion was recovered. It was manually pulverized and electrically sieved before demineralization was done.

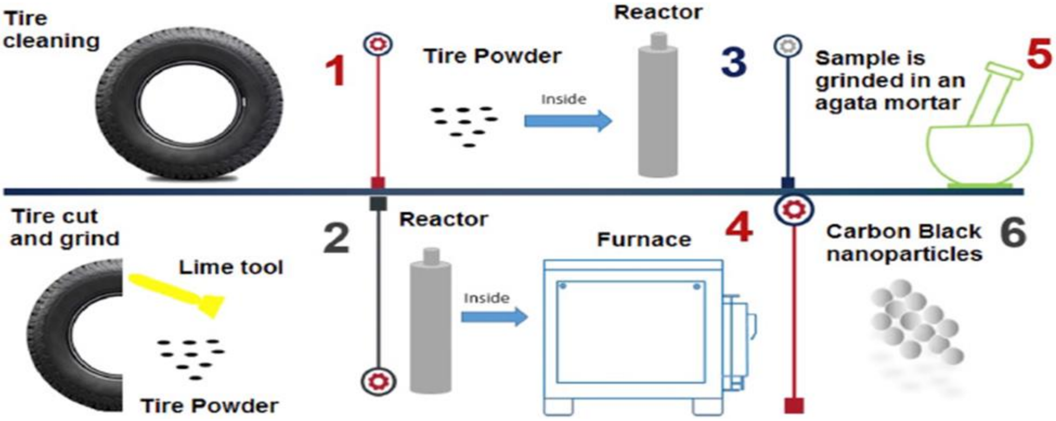

Figure 1.0: Schematic representation of the carbon black nanoparticles preparative process steps [24].

Sieving of Samples: Using standard (ASTM/BS-410) sieving plates of mesh No. 400, 300 and 100, the carbon black sample (spent tire) sieved consecutively [23]. The particle sizes of -400, +400 and +300 meshes which correspond to < 37µm, 37µm and < 44µm respectively was separated and mesh with the least particle size (< 37µm) is collected while the mesh with higher particle sizes (the other two) is further reduced to obtain more grams of the least particle sizes.

Acid Demineralization: An acid demineralization procedure was used at room temperature to reduce the amount of inorganic impurities (metals) and eliminate unwanted materials (ash). 80ml of concentrated hydrochloric acid was added to the pigment sample (carbon black) weighed 40g in a 250ml conical flasks. The sample was demineralized for twenty-four hours, which was deemed to be an adequate duration to allow the demineralization process to proceed unhindered. The sample was filtered and completely rinsed with distilled water after 24 hours to get rid of any remaining acid. After that, the sample was dried for 7 hours at 110°C in an oven [23]. Acid-basic chemical pretreatment of waste tires is another alternative for the elimination of inorganic additives such as silica and metals, among others [25]. The sample of dried tire carbon black was pulverized once more to get rid of any remaining unwanted particles that was collected in the process.

Ink production: 18 (wt%) modified starch used as thickening agent was dissolved with water as solvent and stirred to obtain viscosity, an additive stearic acid was added to the mixture and stirred for 30min using magnetic stirrer to obtain varnish. The prepared pigment (25 wt%) from waste tire was mixed with the varnish and stirred for 30 min using magnetic stirrer to obtain a homogenous mixture, 10ml of Isopropyl alcohol was then added to blend the modified starch and stearic acid by lowering the viscosity of the ink mixture and help achieve a uniform distribution of components. The prepared ink was then tested for its properties [2].

Physical Properties Characterization: Visual comparison was used to determine opacity while the viscosity was determined using a syringe and stopwatch [2]. The ink was used to write on a whiteboard and the drying time was measured. The erasability of the ink was also determined after 5 mins and 24 hrs while a 5 m distance was used to test the eligibility of the ink. Adhesion property of ink was carried out by applying on a whiteboard and allowed to dry for 24 hours. Two sets of lines, one crossing perpendicularly over the other was drawn on the board. An adhesive tape was pressed firmly with the thumb covering all the interactions of the perpendicular line. The adhesive tape was held at its loose ends and forcibly removed from the surface. Removal of more than 50% of the square lines of the ink sample indicates a poor adhesion and erasability. All physical characterizations were done in triplicates. The parameters for the best ink was then optimized Osemeahon *et al*., (2020) [2].

Pigment characterization: Ultimate analysis was used to determine the elemental composition of the carbon black [26]. It measures the percentages of key elements: carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulfur (S), and sometimes ash. This analysis helps in understanding the energy content, combustion characteristics, and environmental impact of the material. The results are essential for optimizing processes like combustion, gasification, and pyrolysis, as well as for ensuring regulatory compliance regarding emissions.

Fourier Transform Infrared (FTIR): spectroscopy was used in identifying the chemotypes and functional groups in the tire carbon black pigment. It helps explain the molecular structure and composition of the sample.

FTIR analysis of tire carbon black particles reveals functional groups on the surface [24], such as hydroxyl and carbonyl groups, which are crucial for determining the physicochemical processes on the outer surface layers. It also helps determine acceptable purity levels and surface modification of carbon black.

Image of pigment sample obtained during preparation.

Figure 2a, b & c: Shredded pieces of tire before, pyrolysis image of sample after pyrolysis and dried pigment sample after demineralization

Figure 3a & b: Image of ink produced

RESULTS AND DISCUSSIONS

The properties of the inks produced are given in **Table 1**.

pH: The pH and other chemical characteristics of the ink are important in terms of its compatibility with the construction materials of the print head [27]. The compatibility means that the ink should damage neither the print head materials nor the adhesive bond between different head parts and also that the print head materials should not leach out any material to change the ink composition or properties in any way affecting the stability, jetting or ink performance on the substrate (Khan, 2016). The pH was determined to be 5.3 **Table 1**. The pH slightly alkaline is less acidic and suitable for good ink to surface interaction [28].

Surface tension: The optimum surface tension for jetting and printing is determined by the surface energy of the channel of the nozzles and that of the front face of the printing surface in such a way that the ink does not ooze out and wet or dirty the front face, but has the maximum force to wet the channel to maintain the proper meniscus is maintained [2]. This requires both static and dynamic surface tension to be right (Khan, 2016). This study shows the surface tension of 57.8 mN/m was obtained as seen **Table 1**. This is suitable for printing as most of the areas to be printed accept the ink film and the not to be printed areas have a hydrophilic structure allowing printing easier [28].

Viscosity: The viscosity (or more precisely the rheology) determines the fluid dynamics for the specific design of the print head geometry, e.g. the sufficient supply of the ink for printing, otherwise delayed Start-up, ink-starvation and massive nozzle dropout can occur [2]. Viscosity is far from enough to know the rheology profile of the ink. Even if the rheology profile is known, it is still difficult to predict the fluid dynamics and drop formation due to the complicated geometry of the ink pathway and the driving waveform [19]. Nonetheless, viscosity provides a starting point and gives the formulator something to start with (Khan, 2016) [29]. The Viscosity (ASTM D4040-81) was determined and obtained to be 38.9 (Pa.s./25° C) **Table 1**, which supports printing. This was found to be closer in range (36.11) to the study conducted by Osemeahon *et al.*, 2020 [2].

ISSN No. 2321-2705 | DOI: 10.51244/IJRSI |Volume XII Issue I January 2025

Drying time: The Spent tyre soot inks demonstrate comparatively good adhesion, opacity as compared to the study by [2]. It is also observed that there is an increase in viscosity which decreases the drying time as seen in **Table 1**.

Table 1: Physical Property Characterization of the produced ink.

Property	**Value**
pH	5.30
Surface tension (nM/m)	57.80
Viscosity (Pa.s./25° C)	38.90
Drying time (s)	5.43
Opacity	+ Ve
Tack	+ Ve
Gloss	Better
Length	Optimum
Stability	Good
Eligibility	Good
Adherence	Good
Rub Resistance	Good

Other properties: The lampblack and Spent tyre soot inks demonstrate comparatively better goss and optimum length. As shown in **Table 1**, the Stability, Eligibilty, Adhesion, Rub Resistace are however found to be good. This finding were in line with t study has conducted by Osemeahon *et al*., 2020 [2].

Temperature's Impact on Printing Performance: Viscosity is the most important factor that define the printing ink as an ideal one for the use in printing industry. The type of ink an ink chemist can start by looking at right from the onset is the viscosity of an ink for a particular situation. Since viscosity is sensitive to temperature change, it is imperative to note that a small change in temperature as in going from room temperature to that of the printer could greatly affect viscosity and consequently the performance of the ink. The result obtained is shown in **figure (4)**.

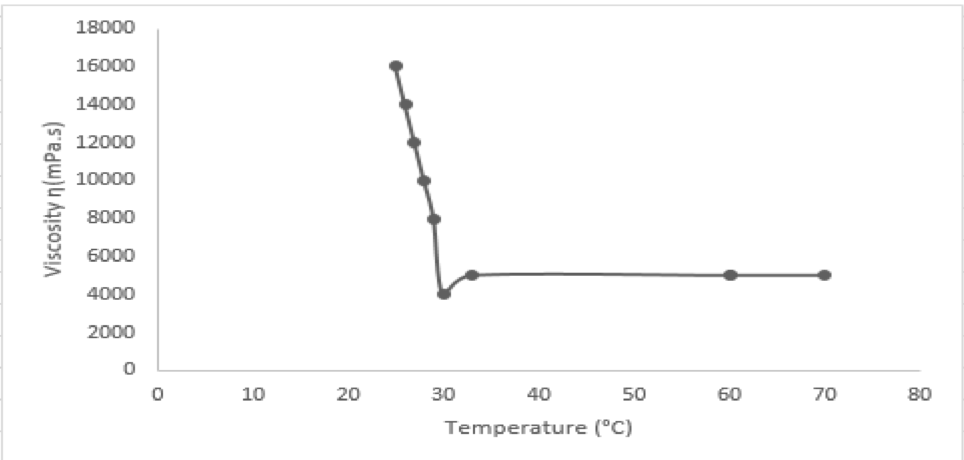

Figure 4: Ink viscosity vs temperature.

ISSN No. 2321-2705 | DOI: 10.51244/IJRSI |Volume XII Issue I January 2025

The effect of pigment concentration on drying time: The drying time of the ink is a function of its viscosity. The relationship between the mass of pigment used and the drying time in this study is illustrated in **figure 5**, and it shows an inverse relationship. The presence of more particles results in a higher mass per unit of volume and therefore a higher density lower rate of evaporation [30].

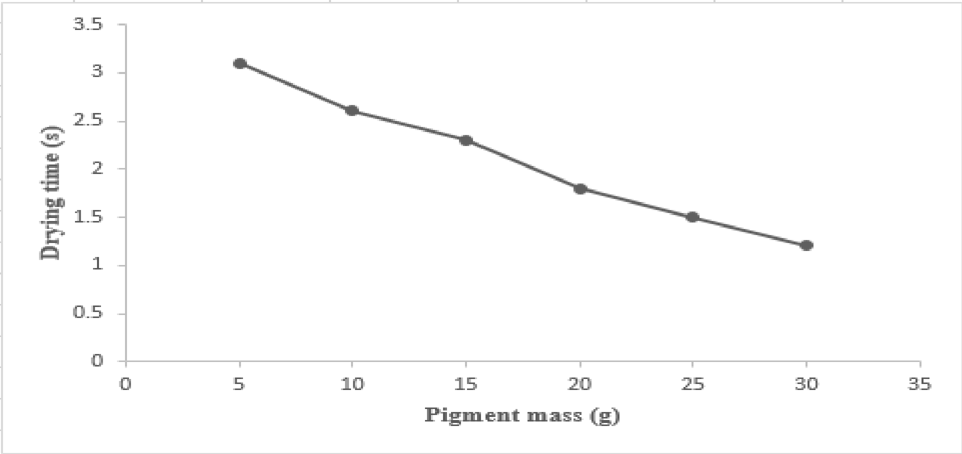

Figure 5: Relationship between pigment mass and the drying time of the Ink

Table 3: Effect of solvent ratio on Physical properties of Ink from lampblack

Samples	**Ethanol (ml)**	**Water (ml)**	**Pigment (g)**	**Drier (s)**	**Viscosity (s)**	**Drying time(s)**
A	5	30	1.5	0.15	8.50	65.07
B	10	25	1.5	0.15	7.20	52.65
C	15	20	1.5	0.15	3.52	42.02
D	20	15	1.5	0.15	2.15	30.69
E	25	10	1.5	0.15	1.72	25.01
F	30	5	1.5	0.15	1.15	14.43

The effect of solvent ratio on the property of the ink produced is shown in **Table 3** the result shows that the viscosity decreases with increase in diluent ethanol concentration which can be explained as a result of decrease in molecular weight resulting to more free volume between liquid particles hence solvent evaporate easily Waje *et al*., (2005). [31]. Sample A has the ratio quantity of 1:5 of ethanol to water hence it gave the highest viscosity as a result of higher intermolecular forces between the liquid particles, rate of evaporation decreases. This happens because intermolecular forces make it less likely for the solvent molecules on the surface to escape thereby increasing drying time while sample F is of the least viscosity (1.05) and is lower as comparable to (1.21) Osemeahon *et al*., 2020, obtained by resulting to free volume caused by rate of diffusion[32].

Table 4: Ultimate analysis results.

Element	**Wt. %**
Carbon	82.91
Hydrogen	6.26
Oxygen	9.17

Sulphur	1.00
Nitrogen	0.90

Ultimate analysis The Elemental analysis was carried out to determine the basic elemental composition of the waste tire material, major elements were identified and quantified as shown in Table 4.1. The highest composition was observed in carbon at 82.919 wt. %, hydrogen 6.266 wt. %, and oxygen 10.179 wt. % this confirms the rich hydrocarbon content of the material. Trongkaew *et al.*, 2011, also observed carbon composition above 80 wt. % these shows waste tires to be rich in carbon materials.

FTIR analysis: The FTIR analysis was carried out to determine major peaks of functional groups present on the waste tire material to be used as pigment, the FTIR spectra of the calcined waste tire powder is shown in *Figure* 6 and identified major peaks as C-H, C=O, C-H and OH identified at 3000 cm^{-1}, 1700 cm^{-1}, 1000-1500 cm^{-1} , and 3500-3600 cm^{-1} respectively, the presence of C-H and C=H stretches confirms the high amount of carbon and hydrogen observed from the analysis and confirms its hydrocarbon composition. Taleb *et al.*, 2020 studied pyrolysis of waste tire and observed similar functional groups on waste tire powder although the o-H disappeared after heating at 500^{o}C.

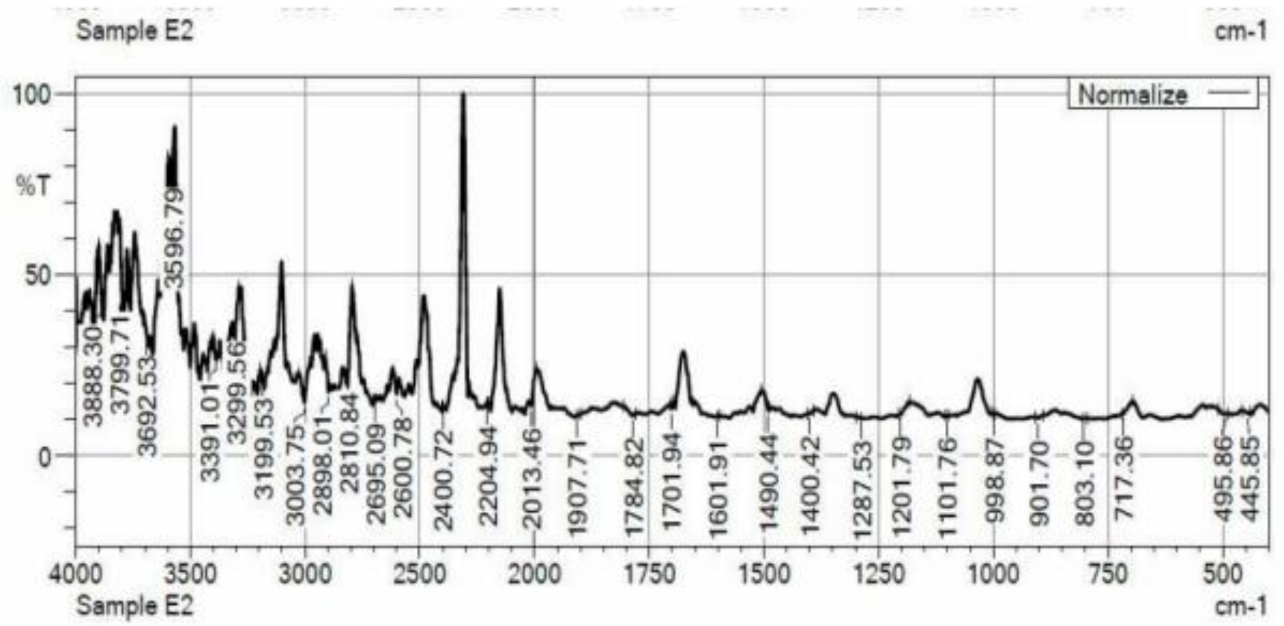

Figure 6: FTIR analysis result showing the major peaks.

Conclusion and suggestions: This work have demonstrated the production of Carbon black from locally sourced carbonaceous waste such as spent tyre, optimization, and application of black offset printing ink using waste tire. From this research work it can be seen that offset printing ink can be produced in Nigeria even from waste materials like spent automobile tire, thus converting waste to wealth. The pyrolysis of waste tires for carbon production may have environmental implications, these can be mitigated through proper waste management, technological innovations and commitment to sustainable practices [26]. The formulated ink from carbon black demonstrated a high degree of compliance to the imported ink in terms of viscosity, opacity, adhesion, eligibility and erasability test but poor drying time. The use of waste tire carbon provides a cost effective and environmentally friendly solution for printing ink production in industrial scale. This research was directed on the development of quality products, non-hazardous to the environment but responsive to market demand as an impact to the environment. Material recycling has helped in the identification of re-use and management of the domestic and industrial wastes. Notably, they are eco-friendly, sustainable, non-hazardous and bio-degradable in nature. The work contributes to waste management and innovative ink production. A good suggestion would be the establishing of collection centers of waste tires for recycling to ensure a consistent supply of raw materials and the collaboration with companies.

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