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Artigo

An Innovative and Accessible Chemical Approach to Bisphenol Identification on Plastic Surfaces

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Uma Abordagem Química Inovativa e Acessível Para a Identificação de Bisfenol em Superfícies Plásticas

Abstract: O atual estilo de vida arquitetou-se gradualmente sobre materiais sintéticos feitos de uma ampla gama de polímeros à base de óleo, e isso contribuiu de alguma forma para o desenvolvimento global. Sob a perspectiva econômica para aprimorar as características e aplicações dos plásticos, os cientistas fizeram extensos testes com moléculas conhecidas e novas para atuar como dependências químicas, obtendo um tremendo sucesso com o bisfenol A (BPA). Ao longo dos anos, no entanto, as agências mundiais de vigilância em saúde discutiram os efeitos perigosos do BPA nos seres humanos com base em relatórios científicos disponíveis na época. Dessa forma, o presente trabalho comprovou a viabilidade do teste da mancha de cloreto férrico como detector de compostos fenólicos liberados a altas temperaturas de itens de plástico, o que serve como método indireto para identificação de BPA. Portanto, esta pesquisa é uma nova maneira de reconhecer compostos fenólicos nocivos em itens de plástico comercializados usando uma abordagem química simples e econômica.

Keywords: Bisfenol A; BPA; Cloreto férrico; Identificação fenólica; Plástico; Teste de mancha.

Resumo

Abstract: The current lifestyle has gradually architected itself upon synthetic materials made from a wide range of oil-based polymers, and this has contributed somehow to global development. Under the economic perspective to enhance plastic features and applications, scientists took extensive tests with well-known and new molecules to perform as chemical addictions, thereby, having tremendous success with bisphenol A (BPA). Over the years, however, worldwide health surveillance agencies discussed the hazardous effects of BPA on humans based on scientific reports available at that time. Accordingly, the present paper proved the viability of the ferric chloride spot test as a detector for phenolic compounds released at high temperatures from plastic items, which serves as well as an indirect method for BPA identification. Therefore, this research is a new way to recognize harmful phenolic compounds in commercialized plastic items using a simple and cost-effective chemical approach.

Palavras-chave: Bisphenol A; BPA; Ferric chloride; Phenol identification; Plastic; Spot test.

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An Innovative and Accessible Chemical Approach to Bisphenol Identification on Plastic Surfaces

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1. Introduction

Organic compounds have been used by civilizations dating back to ancient times. However, an academic understanding of their chemical properties emerged much later in the mid-15th and 20th centuries. [1] Since then, there have been significant advances in methodologies for the identification and purification of organic compounds, and in the synthesis thereof, which contribute to a wide variety of organic molecules we know of today. Over the years, on the other hand, scientists have observed that some of these chemicals lead to harmful effects on human health, including reduced fertility and endocrine disruption in humans. [2,3]

In the 21st century, plastic plays a central role in manufacture and in ordinary life. These synthetic polymers derived from oil are commonly found in a diversity of materials and objects, including disposable cups, feeding bottles, and food packages. Some types of plastics also contain chemical additives that are used to achieve desired characteristics in the product. Polyvinyl chloride (PVC) plastics, polystyrene (PS) plastics, and others usually contain toxic additives in their formulation, such as bisphenol A (BPA). [4] In 2015, it was estimated that 8300 million metric tons (Mt) of virgin petroleum-based polymers were destined to the production of resins, fibers, and additives, of which PVC and PS contribute 15% to global production and 6.5% in the packing industry. [5]

Bisphenol A was first described by a Russian chemist, Alexander P. Dianin, in 1891 and synthesized in 1905 by Thomas Zincke, at Universität Marburg, from the condensation of propanone with two phenol molecules in low pH and at high temperatures (Figure 1). [2] In 1938, a British chemist, Charles Dodds, detected estrogenic properties of bisphenol A because of the presence of hydroxyl groups in the para position, which is quite similar to estradiol. [2] In 1953, Daniel Fox and Hermann Schell discovered BPA capacity for performing cross-linkages during the polymerization arising to polycarbonate, and, in 1957, the USA started the large-scale production of bisphenol A. [2,4] In 2008, the Food and Drug Administration (FDA) released a draft report attesting that BPA remains safe in food contact material; however, an institutional subcommittee raised a few questions about whether the review had adequately considered most scientific data available. In 2012, the FDA amended its regulations to no longer allow the use of BPA-based for polycarbonate resins in baby bottles and sippy cups, and the epoxy resins as a coating in packaging for infant formula in 2013. [6,7]

Most studies reporting BPA identification support the idea through instrumental analytic methods as well as High-Pressure Liquid Chromatography (HPLC), Mass Spectrometry (MS), or an alternate spectrophotometry analysis. [8,9,10] Although in our bibliography review there were myriad approaches for BPA characterization, no article discussed the implementation thereof for a layman in the subject. Accordingly, the group proposed the use of a ferric chloride spot test, which is well established in the literature for a qualitative phenol identification (Figure 2). We extrapolate this stand in a simple, quick, and cost-effective chemical approach to bisphenol recognition on plastic surfaces; therefore, it will perhaps be configured as another important tool for surveillance agencies to maintain public health.

2. Materials and Methods

The experiment was designed to test a) glass beaker, b) polypropylene disposable cup, c) polystyrene disposable cup, d) free BPA canister, e) feeding bottle A and f) feeding bottle B, employing a 5% w/v ferric chloride solution (Sigma-Aldrich 7705-08-0) in ethyl alcohol 80% v/v (Sigma-Aldrich 64-17-5). The standard methodology is to place two drops of ferric chloride onto a piece of filter paper and instantly lay it against the external plastic surface, in such a way that contact with the material occurs for ten seconds, which is enough time for the reagent to dry. At high temperatures, the group heated water (98°C) and filled the plastic item to 4/5 of the total volume, and after

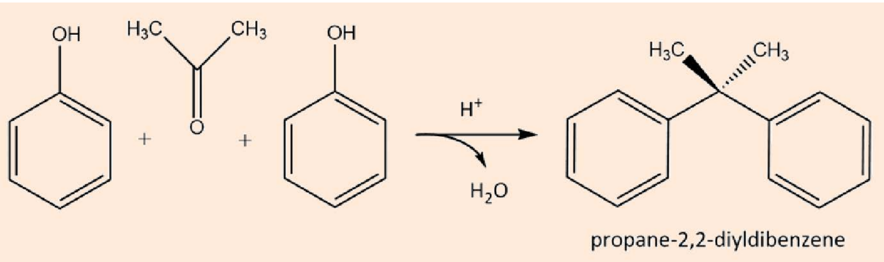

Figure 1. Bisphenol A synthesis reaction. Combination of two phenol molecules gather with a propane in low pH, and under high temperatures resulting in bisphenol A and water as products of the synthesis

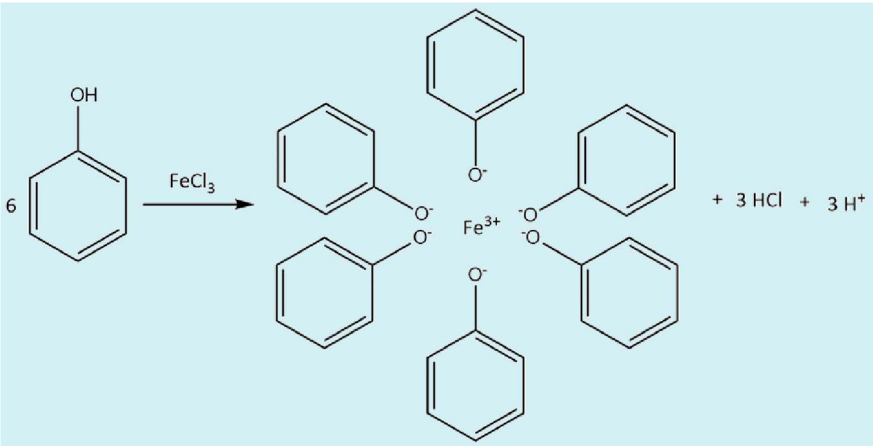

Figure 2. Chemical aromatic test reaction. There is the combination of phenolic molecules with ferric chloride, which is dissociated in the alcoholic solution. The ions iron (III) are coordinated with six phenolic molecules ensuring the reddish-brown coloration

ten seconds, the ferric chloride spot test was performed. The qualitative analyses carried out in this experiment were based on the color complex.

3. Results and Discussion

The group focused on daily plastic products commonly adopted in food packaging or food apparatus to apply the ferric chloride colorimetric assessment, which uses color changes to identify phenolic compounds in the plastic matrix through ferric complexation therein. We worked with a polypropylene disposable cup, a polystyrene disposable cup, a free BPA canister, feeding bottle A, and a feeding bottle B; we also tested a glass beaker to parametrize other results.

The filter paper pieces displayed in Figure 3 reveal the above objects analyzed four consecutive times at room (23°C) and high (98°C) temperature to guarantee an assertive statistical analysis from the presented results. Besides, whether three of the four tests had the same label (green or red), which reflects color pattern through a simple side by side comparison, led the group to conclude the presence or not of phenol complexation with ferric on the plastic surfaces and detect those objects with high chances to present bisphenol as an addictive in manufacturing composition. The first column illustrates the glass beaker filter paper coloration after ferric chloride reaction at room temperature, where we can observe the orange color that correlates with the reagent pigmentation dropped on its surface. At high temperatures, the group had heated water and poured inside the object, holding ten seconds to an efficient heat distribution, to then remake the same methodology as discussed previously; there was no visual detectable change on filter paper orange pigmentation compared to those at room temperature. Moreover, there are no strong marks to contrast the difference in these two distinct environment conditions justifying the bottom red label in all the tests. On the other hand, the polypropylene disposable cup presented a clear undulation because of plastic surface texture in the last analysis at high temperature, and it had a significant color change in parallel to the filter paper at room temperature. Although tests one to three still present a light imprinting from the plastic surface onto the filter paper pieces, the initial orangish-yellow color was dramatically transposed to a reddish-brown one, corroborating the positive result in all four analyses. Under this perspective, the stripes in polystyrene samples, which also correspond to the matrix texture, appeared in all the tests at high temperature in contrast with polypropylene analyses. Therefore, the expressive color divergence attests unmistakably to a positive result.

In the other display, there is the BPA-free canister that in the first test presented a negative result. Samples two to four have strong marks and, in contrast to disposable cups, there is only a single line according to the smooth object texture and

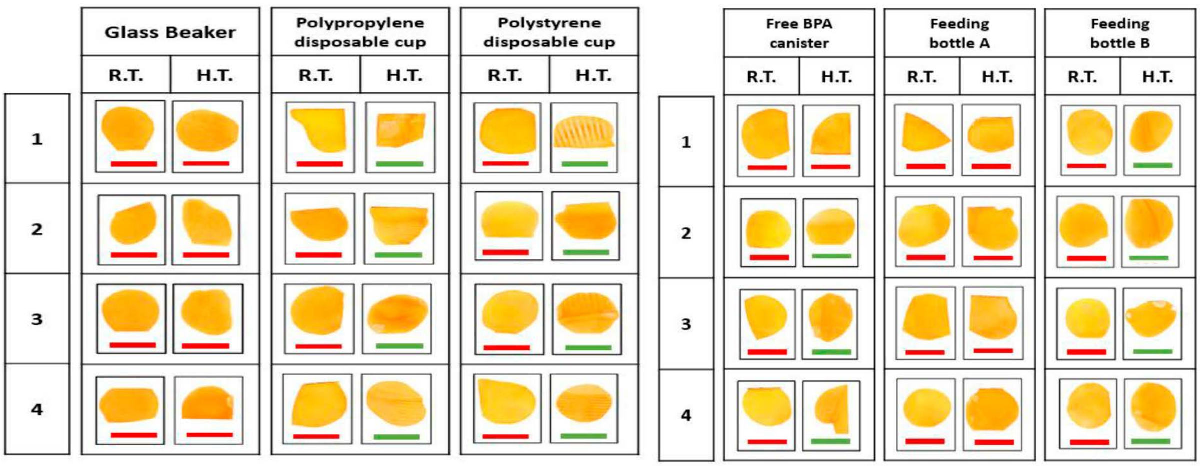

Figure 3. Display of filter paper photography for ferric chloride spot tested on a) glass beaker, b) polypropylene disposable cup, c) polystyrene disposable cup, d) free BPA canister, e) feeding bottle A, and f) feeding bottle B. Each product was consecutively tested four times under two different conditions: room (R.T.) and high temperature (H.T.) – 23 and 98°C, respectively. Results interpretations followed a red and green label to indicate negative and positive assessment

this strong mark is a result of direct contact with the corners of the material. This observation leads to labeling those tests as a positive, green label. The feeding bottle A presents a consistent result since there was no contrast in coloration between samples evaluated at room and high temperature. For this reason, all the samples received a red label. The other polypropylene feeding bottle had an effective imprinting in those tests at high temperature in agreement with the juxtaposition of two-environment tested. It is also possible to note some white circle forms in the third analysis at high temperature, deriving from water vapor that contributed to the ferric chloride's seeping through the filter paper; however, it does not affect the contrast in coloration between the initial orangish-yellow and reddish-orange, leading to a straight positive conclusion.

The experiment is based on the extrapolation of molecules' physical property to migrate from one immiscible solvent to the other at equilibrium conditions measured by the partition coefficient (κ) thereof, dictating the permeability of molecule in passing from one phase to another. Besides, the heated water strategy relies on the dependence of the partition coefficient on temperature as reported by Congliang *et al.* 2007. [11] Accordingly, we expected the diffusion of bisphenol A (logκ = 3.40) in the plastic matrix, when the heated water was inside of the item, toward the surface once there was the decrease of the partition coefficient. [12] The BPA leached from plastic into liquid food relies on the diffusion of additive surplus after the manufacturing process and in polycarbonate plastics through polymer hydrolysis. [13]

Another relevant concern about working with the manufacture of plastics is the myriad of organic and inorganic compounds applied in pigmentation that, in some instances, could chemically interact with ferric chloride and jeopardize the method used in the present paper. However, the essential industrial organic molecules applied do not have a free hydroxyl group to interact with $FeCl_3$, which still ratifies the results. The extensive dyes used in polystyrene and polypropylene pigmentation belong to the family of anthraquinone, azo, isoindoline, benzimidazole, diketopyrrolopyrrole (DPP), BONA lake, quinacridone, and phthalocyanine. If plastic coloration is a strict result of a resin coating, it is simple to scrape this coating off, uncovering the polymer surface, and the tests can proceed. [14] We reinforce that the reasoning for molecules' coloration arises from the hyperconjugation present between double-bound or outer shell electrons, which contributes to the stability of the system, decreasing the ground and excited energy levels and resulting in the absorption of lower energetic wavelengths. Besides, the dye associated with the polymer is based on van der Waals forces. [15]

The ferric chloride analyses are well-established by the literature, whereby a red coloration is a positive indicative for the reaction in accordance with Figure 3.[16] Therefore, the ferric complex is absorbing light in ~ 500 to 485 nm as reported by Wesp and Brode, 1934, who conducted an absorption spectra experiment because of phenol and ferric chloride interaction in aqueous solution. [17] This spectrum corresponds to metal to ligand charge transference (MLCT) between t_{2g} and π* ligand orbital since the free hydroxyl group has as characteristic to be a π ligand-receptor (Figure 4). Besides, this scenario is favorable in complexes with d^6 orbital metals configurations, such as Fe^{3+}. [18]

Ferric chloride complexation in polystyrene-based manufactures matched information available on the Internet; on the other hand, positive results in polypropylene plastics were unexpected and led us to support the idea thereof that there is the addition of correlate species to bisphenol A, which the FDA did not prohibit as a substitute for infant products. [19,20] Accordingly, the tests in polypropylene and polystyrene disposable plastic cups, as well as feeding bottles, attested a positive result, save feeding bottle A. Even though the canister has a "BPA free" tag, the consensus from analyses drove to a positive interpretation, thereby corroborating BPA substitution, for instance, for bisphenol S (BPS) and bisphenol F (BPF). [21] Because of structural similarities with bisphenol A, these alternatives also show endocrine disruption effects, and they keep the free hydroxyl group to react with $FeCl_3$. However, only polystyrene plastic had the strongest marks imprinted on filter paper pieces even when directly compared to polypropylene disposable cups. To sum up, this may suggest a higher concentration of BPA in these manufacturers' products, but some further quantitative tests should be taken.

As described above, other phenolic species can react with ferric chloride and raise a doubt about the limitations of BPA identification

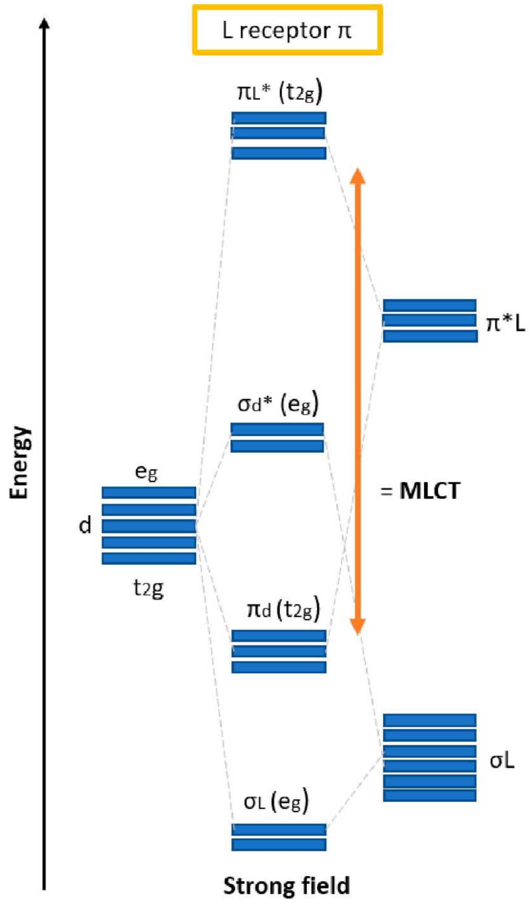

Figure 4. Energy diagram of molecular orbitals for the complex by phenol and ferric chloride interaction. On the left there are five d molecular orbitals of Fe^{3+}, and on the right the phenol molecular orbital distribution. The orange arrow indicates the metal to ligand charge transference (MLCT) between t_{2g} and π* ligand orbital, which is responsible for the reddish-brown color in the end. Adapted from the original[18]

methodology because the spot test is based on free hydroxyl groups. Perhaps, the canister complied with surveillance agencies' legislation, as well as it may use another chemical addictive according to our results. Under this perspective, all the manufacturers that positively tested exhibit a free hydroxyl group and high probability to be associated with an aromatic structure. To precisely affirm this, other analytical methods will be necessary, such as absorption spectra, chromatography, and NMR. Having the results on hand, we will be able to validate the interpretation present in this paper.

Ferric chloride spot test is a simple, quick, and cost-effective chemical approach to bisphenol recognition on plastic surfaces. The process requires no expertise: two drops of ferric chloride solution must be dripped on a piece of filter paper – it is strongly advisable to use only this amount of reagent since a high concentration of the chemical does not allow its diffusion through the paper, and this increases difficulty in visualizing a color change when it is the case. Besides, the soaked filter paper must be laid following the natural shape of the plastic item; otherwise, a strong mark can indicate some paper folding, thereby concentrating ferric chloride on only one site, leading to a false positive. For that reason, a minimum of three tests with the same object need to be conducted so that the item corners may be out of the testable scope. Also, the solution needs agitation before each test to guarantee homogeneity. Table 1 is a market research of the average price of the kit: the reagents had Sigma-Aldrich and the apparatus Fisher scientific pricing, totaling US$ 3.50, which can surely last for at least 50 tests.

While performing the ferric chloride spot test, attention is necessary since the chemical is corrosive and may cause irritation in contact with eyes or skin; overall, it has moderate health risks on handling

Table 1. Ferric chloride kit for price estimate based on the reagents and apparatus for the test

Name/[CAS]	Price (US$)	Kit price
Ferric Chloride [7705-08-0]	32.00 (1 kg)	1.5 g = US$ 0.05
Ethyl alcohol [64-17-5]	50.85 (1 L)	30 mL = US$ 1.53
Filter paper 70 mm	8.00 (100 units.)	10 units. = US$ 0.80
Disposable pipette 1 mL	29.15 (500 units.)	1 unit. = US$ 0.06
Neck round bottle 30 mL	15.88 (10 units.)	1 unit = US$ 1.06

[22]. For disposal, either contact the local hazardous waste disposal company or render it safe for disposal by carefully neutralizing it with a spoon of sodium bicarbonate – If there is a sludge, it should be allowed to settle. After that, the liquid is transferred, further diluted with water, and discarded down the drainpipe. The sludge and the filter paper pieces may be collected in plastic bags to be disposed of as required by local waste authorities. [23]

4. Conclusions

The present analyses validate ferric chloride as an effective qualitative test to detect phenolic compounds released at high temperatures from plastic items. Moreover, these analyses are easy to postulate negative or positive results, by which this methodology configures as a simple indirect to bisphenol identification. Within this project, a new way comes up to detect harmful compounds released from certain oil-based polymers, with the intention of minimizing health risks, as a useful tool for surveillance agencies to maintain public health and people's awareness of daily product toxicity.

References

[1] Beserra, M. R.; de Araújo Schiavini, J.; Rodrigues, W. C.; Pereira, C. D. S. S. Bisfenol A: Sua utilização e a atual polêmica em relação aos possíveis danos à saúde humwna. *TECCEN* **2012**, *5*, 37. [CrossRef]

[2] Souza, R. R. D.; *Tese de Doutorado*, Universidade de São Paulo, 2011.

[3] Eladak, S.; Grisin, T.; Moison, D.; Guerquin, M. J.; NTumba-Byn, T.; Pozzi-Gaudin, S.; Benachi, A.; Livera, G.; Rouiller-Fabre, V.; Habert, R. A new chapter in the bisphenol A story: bisphenol S and bisphenol F are not safe alternatives to this compound. *Fertility and Sterility* **2015**, *103*, 11. [CrossRef] [PubMed]

[4] Bernardo, P. E. M.; Navas, S. A.; Murata, L. T. F.; Alcântara, M. R. D. S. Bisphenol A: o uso em embalagens para alimentos, exposição e toxicidade – Uma revisão. *Inst Adolfo Lutz* **2015**, *74*, 1. [Link]

[5] Yeo, J. C. C.; Muiruri, J. K.; Thitsartarn, W., Li, Z.; He, C. Recent advances in the development of biodegradable PHB-based toughening materials: approaches, advantages, and applications. *Materials science and engineering* **2017**, *92*, 1092. [CrossRef] [PubMed]

[6] Food and Drugs Administration. Bisphenol A (BPA): Use in food contact application. Available in: <https://www.fda.gov/food/food-additives-petitions/bisphenol-bpa-use-food-contact-application>. Accessed in: 5 May 2020.

[7] Food and Drugs Administration. Bisphenol A (BPA). Available in: <https://www.fda.gov/food/food-additives-petitions/bisphenol-bpa>. Accessed in: 5 May 2020

[8] Spagnuolo, M. L.; Marini, F.; Sarabia, L. A.; Ortiz, M. C. Migration test of bisphenol A from polycarbonate cups using excitation-emission fluorescence data with parallel factor analysis. *Talanta* **2017**, *167*, 367. [CrossRef] [PubMed]

[9] Biles, J. E.; McNeal, T. P.; Begley, T. H.; Hollifield, H. C. Determination of bisphenol A in reusable polycarbonate food-contact plastics and migration to food-simulating liquids. *Journal of Agricultural and Food Chemistry* **1997**, *45*, 3541. [CrossRef]

[10] Zheng, J.; Zhao, S. Q.; Xu, X. T.; Zhang, K. Determination of bisphenol A in water samples using ELISA determination method. *Water science & technology: water supply* **2011**, *11*, 55. [Link]

[11] Congliang, Z.; Yan, W.; Fuan, W. Determination and temperature dependence of n-octanol/water partition coefficients for seven sulfonamides from (298.15 to 333.15) K. *Bulletin of Korean Chemical Society* **2007**, *27*, 1183. [Link]

[12] Staples, C. A.; Dome, P. B.; Klecka, G. M.; Oblock, S. T.; Harris, L. R. A review of the environmental fate, effects, and exposures of bisphenol A. *Chemosphere* **1998**, *36*, 2149. [CrossRef] [PubMed]

[13] Hoekstra, E. J.; Simoneau, C. Release of bisphenol A from polycarbonate – a review. *Critical Reviews in Food Science and Nutrition* **2011**, *53*, 386. [CrossRef] [PubMed]

[14] SpecialChem. Pigments for plastics: Complete technical guide. Available in: <https://polymer-additives.specialchem.com/selection-guide/pigments-for-plastics>. Accessed in: 5 May 2020.

[15] Lin, L. Adhesion and cohesion phenomena in pigment dispersion. *Surface Coating International* **2000**, *6*, 289. [CrossRef]

[16] Pasto, D. J.; Johnson, C. R.; *Laboratory Text for Organic Chemistry*, Pearson: New Jersey, 1979.

[17] Wesp, E. F.; Brode, W. R. The absorption spectra of ferric compounds. I. the ferric chloride-phenol reaction. *Journal of the American Chemistry Society* **1934**, *56*, 1037. [CrossRef]

[18] Toma, H. E.; *Química de Coordenação, Organometálica e Catálise*, 2a ed., Blucher: São Paulo, 2016.

[19] Goyal, R.; Jain, A.; Singh, S.; *The urban environmental crisis in India: New initiatives in safe water and waste management*, V. 9, Cambridge Scholar Publishing: Cambridge, 2017.

[20] BPA - Bisphenol A – possible effects during fetal development or on newborns. Available in: <https://www.state.nj.us/humanservices/opmrdd/health/bpa.html>. Accessed in: 5 May 2020.

[21] Moon, M. K. Concern about the safety of bisphenol A substitutes. *Diabetes & Metabolism Journal* **2019**, *43*, 46. [CrossRef] [PubMed]

[22] Lab Chem. Ferric chloride solution safety data sheet. Available in: <http://www.labchem.com/tools/msds/msds/LC14380.pdf>. Accessed in: 5 May 2020.

[23] MG Chemicals, Ferric chloride. Available in: <https://www.mgchemicals.com/products/prototyping-and-circuit-repair/prototyping/ferric-chloride-415>. Accessed in : 5 May 2020.