

***In-situ* Fe electro-oxidation to Improve the Synthesis of Mono and Disubstituted Benzimidazoles**

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This paper presents an innovative green organic electrosynthesis to prepare benzimidazoles in methanol media at room temperature starting from *o*-phenylenediamines and benzaldehydes. The main characteristic of this proposal is the *in-situ* Fe electro-oxidation serving as catalyst in the synthetic path of benzimidazoles mono and disubstituted. Anodic linear sweep voltammetry of Fe wire in methanol were used to select the supporting electrolyte among tetrabutylammonium tetrafluoroborate (TBATFB) and tetrabutylammonium hexafluorophosphate (TBAHFP). I vs. E plots pointed toward TBATFB as a better supporting electrolyte due to the fact that Fe presents a lower potential dissolution compared with TBAHFP. Electrolysis at constant potential was performed in a three-electrode undivided cell to prepare two different benzimidazoles (mono and disubstituted) using 1mM TBATFB in methanol. In both cases, good yields and easy purification were achieved. Results indicate that *in-situ* soft electrochemical Fe oxidation produce fresh Fe(III) to act as an effective catalyst for benzimidazoles synthesis and succeed a green chemistry process. Products were characterized by IR, NMR (¹H, ¹³C), and MS. The success of the electrochemical assisted synthesis was compared with a FeCl₃/Alumina previously reported.

Keywords: benzimidazole, *o*-phenylenediamine, Fe electro-oxidation in methanol, organic electrosynthesis

1. INTRODUCTION

Electro-organic synthesis and organic electrosynthesis have been considered as promising approaches to prepare more than a few organic compounds [1]. The most common procedures are the direct electrochemical reaction of some of the reagents, corresponding to electro-organic synthesis.

Good examples are the synthesis of three substituted catechols in the presence of 4-hydroxy coumarin to obtain new coumestan derivatives by direct oxidation of catechols [2] and more recently, the electrochemical dimerization of 4-methylesculetin for the synthesis and kinetic study of a highly-oxygenated dimer was reported as another example of electro-organic synthesis [3]. On the other hand, organic electrosynthesis is characterized by those pathways using the *in-situ* electrochemical preparation of metallic catalyst by a controlled anodic dissolution. For example, the *in-situ* formation of Fenton reagent with Fe and Cu [4, 5], widely used as a powerful oxidation agent. The above mentioned works are just few examples of the huge reported papers dealing with the organic synthesis assisted by electrochemistry and do not intend to bound the infinite possibilities that joining electrochemical techniques with synthetic paths can give [6]. On the contrary it seeks to increase the interest of organic synthesis and electrochemistry experts to create more environmental friendly organic synthesis [7]. In this paper authors assembled three main ideas: to synthesize new benzimidazoles serving as synthetic proteins precursors, to control Fe(III) production serving as a catalyst remaining in solid state and to achieve the most time consuming process at the end of an organic synthesis (traditional or electro-assisted) that is the recovery of the final product with good yield and high purity. The conjunction of these three issues create an innovative electrosynthesis green procedure.

Benzimidazoles are natural and synthetic structures with biological activity [8]. Being heterosystems, they have great interest in medical chemistry and pharmacology [9]. Pharmacological compounds of benzimidazole derivatives are distinguished by their antimicrobial activity [10, 11, 12] having a variety of therapeutic uses including antiparasitic [13], antitumoral [14, 15], antifungal [16], analgesics [17], antiviral [18], antihistamine [19], as well as their use in cardiovascular diseases [20], neurology [21], endocrinology [22], and also as fluorescent chemosensors [23] among other uses. The most common methods applied for the synthesis of benzimidazoles involve reactions between *o*-phenylenediamines and carboxylic acids or their derivatives (nitriles, amidates, orthoesters) in the presence of strong acids [24].

It is common to find catalytic steps in the synthetic path, since the main reaction depends on the electron transfer to oxidize C-H bonds. Catalysts supported on inorganic substrates have received increasing attention lately, assuming that interfacial adsorption of reagents may find the best conditions to progress into benzimidazole structures. A number of methods have been reported for the synthesis of benzimidazoles such as the condensation of *o*-aryldiamines and aldehyde [25]. In recent years, solvent-free synthesis of benzimidazole under microwave irradiation using Yb(OTf)₃[26], KSF clay[26], PPA[26], Na₂SO₄[26], K-10 clay[26], metal halide supported alumina[27], H₂SO₄/SiO₂[28], AMA[29] NaHSO₃[30], and Amberlite IR-120[31] have been reported. Also various oxidative and catalytic reagents such as CAN[32], *p*-TsOH[33], NaHSO₄·SiO₂[34], FeCl₃/Al₂O₃[35], PSPyCl-XAlCl₃[31], H₂O₂/HCl[36], NaY zeolite[37], FeCl₃·SiO₂[38], Co(NO₃)₂/H₂O₂[39], Ni(NO₃)₂/H₂O₂[39], Fe/MgO[40], sulfamic acid[41], Yb(OTf)₃[41], Sc(OTf)₃[41], KHSO₄[41], HfCl₄[41], H₂O₂·HCl[41], FeBr₃[41], Oxalic acid[42], L-proline[42], Glyoxalic acid [42], SDS [42], *N*-halosuccinamide (X= Cl, Br, I)[42], have been used to reach benzimidazole structures. In particular FeCl₃ adsorbed on alumina that has been used as the catalyst in the preparation of benzimidazoles from aromatic aldehydes and *o*-phenylenediamine in DMF [35] is an attractive method that have been

considered as a reference procedure to compare the in-situ formation of Fe(III) on the surface of a pure iron wire during the benzimidazoles synthesis. On the other hand, the interaction between iron surfaces and the already formed benzimidazoles are reported on the corrosion inhibition of Fe in HNO₃ [43].

As above mentioned, the aim of the present study was to synthesize mono- and disubstituted benzimidazoles testing an innovative green procedure assisted by *in-situ* electrochemical Fe oxidation, starting from *o*-phenylenediamine with different benzaldehydes in MeOH. The electrochemical assisted process is expected to get high yields in less time. To validate this proposal the same benzimidazoles were synthesized using the reported method using FeCl₃/Al₂O₃ in DMF [35].

2. EXPERIMENTAL

2.1. General Procedures

All synthesized compounds were detected by thin-layer chromatography (TLC) performed on silica gel F₂₅₄ plates (Merck) using UV light. Melting points were obtained on an Electrothermal 88629 apparatus and are uncorrected. Infrared spectra (IR) were recorded on a Perkin Elmer FT-IR 1600 spectrophotometer. ¹H and ¹³C Nuclear Magnetic Resonance spectra at 200 MHz and 50 MHz, respectively, were recorded on a Varian Mercury 200 MHz Spectrometer in CDCl₃ and/or DMSO-d₆ with TMS as internal standard. Mass spectra were obtained on an Agilent Technologies 5975C MS Spectrometer at 70 eV by direct insertion. The morphology and the surface elemental composition were determined by scanning electronic microscopy (SEM) in a Tescan, VEGA3. The energy dispersive spectroscopy (EDS) was determined in a Bruker QUANTAX 200.

2.2. General Method for Preparing mono- and disubstituted benzimidazoles **1-10**.

In a vial was placed *o*-phenylenediamine (108 mg, 1 mmol), benzaldehyde (106 mg, 1 mmol), MeOH (2 mL), and the synthesized catalyst, FeCl₃/Al₂O₃ (160 mg, 0.1 mmol). The vial was capped and placed into hard stirring for 2 h, the reaction was followed by TLC and finally gravity filtered were performed with several washes of ethyl acetate (3 x 20 mL). The excess of solvent was evaporated at reduced pressure and the solid obtained from evaporation was purified by column chromatography, eluting with petroleum ether and EtOAc[25].

2.3. Electrochemical Method for preparing mono- and disubstituted benzimidazoles.

1 mM supporting electrolyte solution: Tetrabutylammonium tetrafluoroborate TBATFB salt (equivalent 0.0001 mol) was placed in a 200.0 mL beaker and 10.0 mL of MeOH added, the mixture was kept under stirring for 2 minutes with a magnetic stirrer to dissolve the solid. The other supporting electrolyte was prepared in a similar way but this time organic salt was tetrabutylammonium hexafluorophosphate TBAHFB. Both salts were analytical reagents from Merck.

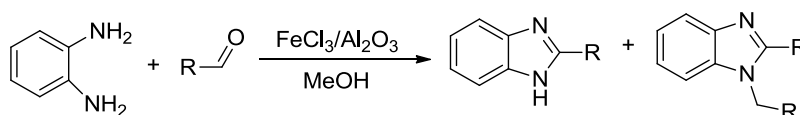
Electrochemical oxidation of metallic Fe wire. The supporting electrolyte was placed in a 50.0

mL undivided electrochemical cell. A typical three electrode system was used, high purity Fe wire was used as working electrode (WE), Pt coil was used as counterelectrode (CE) and Ag/AgCl rod immersed in saturated KCl/MeOH solution as reference electrode. Fe oxidation test was performed on the supporting electrolyte by the anodic linear sweep voltammetry. The experiment was made with a potentiostat-galvanostat from Autolab 320N using Nova software at a scan rate of 100 mV/s, from the open circuit potential (zero current) to a final potential of 2V. Test duration was two minutes and the Fe oxidation onset was identified at 0.55V/Ag/AgCl/Cl⁻_(MeOH). [44]

Electrochemical Synthesis of benzimidazoles. In the electrochemical cell of 50.0 mL the supporting electrolyte was placed (10.0 mL) as well as electrodes: Fe-working electrode, Ag/AgCl/Cl⁻_(MeOH) reference electrode and Pt-counter electrode, then the reaction reagents were added; *o*-phenylenediamine (108.0 mg, 1.000 mmol) and aldehyde (1.000 mmol). A continuous voltage of 0.65 V/Ag/AgCl/Cl⁻_(MeOH) was applied to the working electrode to ensure Fe electro-oxidation using the Autolab potentiostat-galvanostat and stirring constantly for 30 minutes. The reaction was monitored by TLC.

3. RESULTS AND DISCUSSION

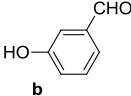
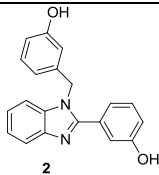
The synthesis of benzimidazoles was carried out with *o*-phenylenediamine and two different benzaldehydes as a starting material, using the base reaction shown in Scheme 1.



Scheme 1. Synthesis of benzimidazoles using FeCl₃/Al₂O₃ catalyst in methanol.

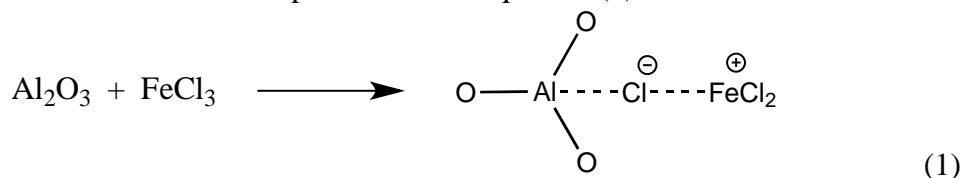
Table 1. Substitutions results and yields in products 1 and 2.

Aldehyde	Product	Yield in 30 min		Grade
		General Method (%)	Electrochemical Method (%)	
 a	 1 3OH-BZ-imidazole	10	90	mono

 <p style="text-align: center;">b</p>	 <p style="text-align: center;">2 4H-BZ-1,3 diol</p>	15	99	di
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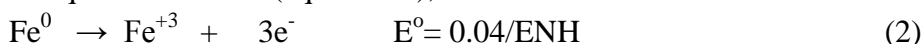
In the first set of experiments, the reactions were catalyzed by $\text{FeCl}_3/\text{Al}_2\text{O}_3$ in MeOH using the aldehydes **a** and **b** respectively (Table 1). The catalyst was prepared by reported method [45], and the reactions were made at normal conditions of temperature and pressure during 4 h to afford compounds **1** and **2** (Table 1). Results presented in this work concern two different process: (1) alumina supporting Fe(III) prepared by ferric chloride impregnation in acetone, to yield a solid having 3.7 wt % Fe [46], and (2) the formation of Fe (III) produced in small quantities by a soft *in-situ* Fe electro-oxidation, sufficient to induce catalytic reaction.

Catalyst formation mechanism. Assuming that the catalyst formation by FeCl_3 supported on alumina involves an initial step as shown in Equation (1)



An interesting result, reported as a corrosion protection of mild steel in 0.5 M H_2SO_4 , that supports this mechanism is that one using a combination of benzene-1, 2-diamine and benzaldehyde with FeCl_3 to *in situ* synthesis of new inhibitor[47]. Also, a Lewis acid, such as Fe_2O_3 compound may assist in the formation of the double bond $\text{C}=\text{N}$ by oxidation process (Fe-catalyzed/mediated oxidative transformation of $\text{C}-\text{H}$ bonds) [48]. Safari et al prepares a one-pot synthesis of 5,5-disubstituted hydantoin derivatives using magnetic Fe_3O_4 nanoparticles as a reusable heterogeneous catalyst [49].

Electrochemical Fe oxidation. Knowing that metallic Fe, as anodic electrode, forms an Fe(III) species in aqueous medium (equation 2),



it was expected that Fe electro-oxidation may also form Fe(III) over the pure Fe wire in methanol. Thus Fe(III) species will appear on the WE to serve as catalyst. Since the selected medium was methanol and no references about supporting electrolyte were found, a convenient potential electro-oxidation of Fe was tested in two organic electrolytes: tetrabutyl ammonium tetra fluoroborate TBATFB and tetrabutyl ammonium hexafluor phosphate TBAHFP. In Figure 1 anodic linear polarization I vs. E curves show the Fe electro-oxidation in methanol at 1mM for each electrolyte. In TBATFB the Fe electro-oxidation presents the onset of the process at lower overpotential (0.50V/Ag/AgCl/ $\text{Cl}^-_{(\text{sat MeOH})}$) and the curve shape suggests that electrode reaction increase its velocity at constant rate as the electrode potential increase (greater slope). On the other hand, TBAHFP showed a larger overpotential for the electro-oxidation onset (1.1V/Ag/AgCl/ $\text{Cl}^-_{(\text{sat MeOH})}$), thus a less

accelerated oxidation rate than TBATFB and more demanding voltage. This result suggest that Fe interface with TBAHFP presents different polarizability probably due to a larger anion size of TBAHFP. Considering that Fe catalysis in $\text{FeCl}_3/\text{Al}_2\text{O}_3$ requires a very small amount of Fe(III), TBATFB was selected as supporting electrolyte to maintain in low level the Fe(III) surface concentration at lower overpotential (less demanding voltage). The chosen overpotential for the bulk electrolysis was $0.65\text{V}/\text{Ag}/\text{AgCl}/\text{Cl}^-_{(\text{sat MeOH})}$.

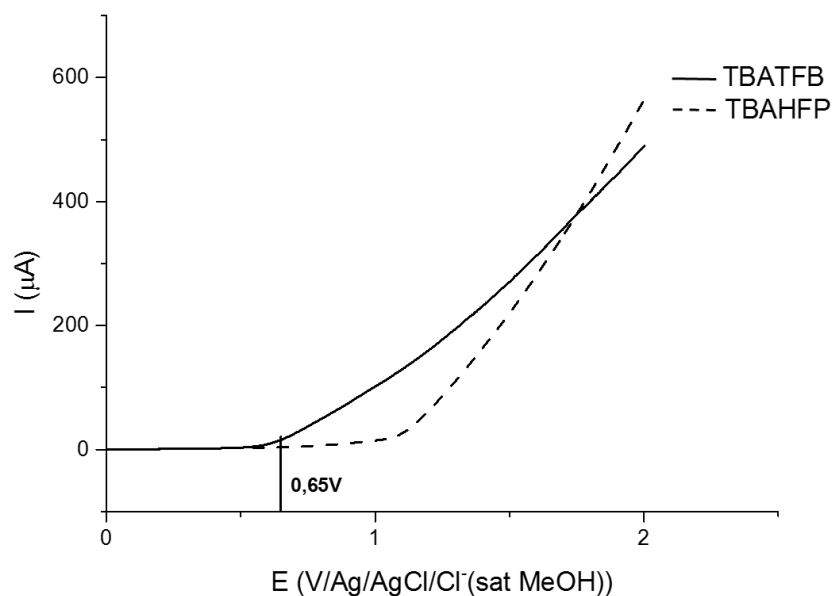


Figure 1. Anodic linear sweep voltammetry of Fe wire in methanol with two different organic supporting electrolytes: TBATFB and TBAHFP 1mM.

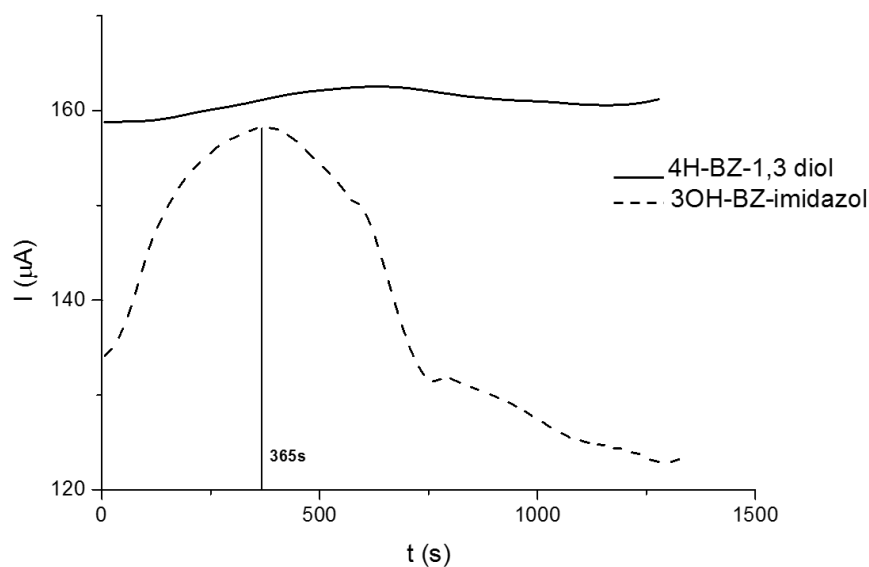


Figure 2. Bulk electrolysis for Fe electro-oxidation at constant voltage $0.65\text{V}/\text{Ag}/\text{AgCl}/\text{Cl}^-_{\text{sat KCl(MeOH)}}$ using TBATFB 1mM as supporting electrolyte.

In Figure 2 the mono and disubstituted benzimidazoles electrochemical assisted synthesis was registered in a I vs t plot representing the bulk electrolysis in the undivided three electrode cell using as working electrode Fe of high purity to produce a solid state catalyst for benzimidazoles synthesis in methanol at room temperature.

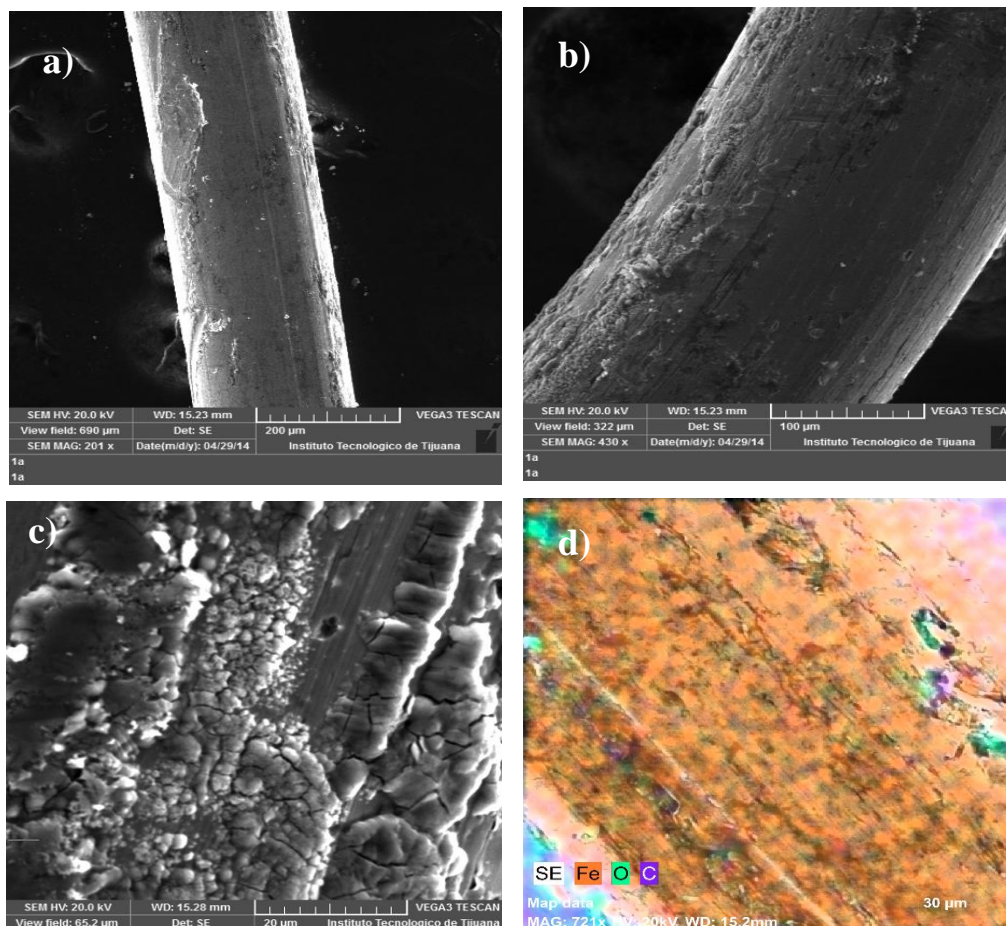


Figure 3. SEM image of Fe wire: a) before electrolysis, b) after electrolysis, c) enlarged image after electrolysis, d) EDS elemental analysis map.

For 3OH-BZ-imidazol the plot suggest a surface passivation after 8 minutes approximately, however yield (Table 1) indicate a 90%. Surface passivation is a well known effect produced by imidazole compounds since they are commonly used as corrosion inhibitors. Instead 4H-Bz-1,3 diol has a constant Fe dissolution during electrolysis and its yield reached 99%. Even though, in both cases the yield was remarkably enhanced with in-situ Fe electro-oxidation compared with that using supported $\text{FeCl}_3/\text{Al}_2\text{O}_3$ catalyst. Mono- and disubstituted benzimidazoles showed from good to excellent yields (see Table 1). It was demonstrated that the electrochemical process is more efficient and faster. Efficiency of the method is due to the controlled production of Fe(III) by soft electrochemical oxidation conditions. The products purification was performed by flash column chromatography and crystallization.

Physical-chemical characteristics of synthesized benzimidazoles

4-(1*H*-benzo[d]imidazol-2-yl)benzene-1,3-diol (**1**): Brown solid. Yield 95 %; mp 260-262 °C; IR (ATR): $\nu = 3552, 3337, 1611 \text{ cm}^{-1}$. ^1H NMR (200 MHz, DMSO- d_6) δ : 10.00 (s, 1H, NH), 7.88-7.84 (d, $J=8.8$ Hz, 2H, Ar-H), 7.59 (m, 2H, Ar-H), 7.24 (m, 1H, Ar-H), 6.49-6.48 (m, $J=2.4$ Hz, 1H, Ar-H), 6.42 (m, 1H, Ar-H), ppm. ^{13}C NMR (50 MHz, DMSO- d_6) δ : 166.0, 165.1, 157.7, 132.7, 127.6, 112.8, 109.7, 108.3 ppm. EIMS m/z ; $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2$, [M] 225.

3-(1-(3-hydroxybenzyl)-1*H*-benzo[d]imidazol-2-yl)phenol (**2**): Brown solid. Yield 97 %; mp 260-262 °C; IR (ATR): $\nu = 3250, 2915, 2750, 1622, 1245, 1209 \text{ cm}^{-1}$. ^1H NMR (200 MHz, DMSO- d_6) δ : 9.80 (s, 1H, OH), 9.44 (s, 1H, OH), 7.74-6.38 (m, 12H, Ar-H), 5.50 (s, 2H, CH₂) ppm. ^{13}C NMR (50 MHz, DMSO- d_6) δ : 157.7, 157.5, 153.2, 142.6, 138.3, 135.8, 131.2, 129.8, 122.6, 122.1, 119.4, 119.2, 116.9, 116.6, 115.9, 114.4, 112.6, 111.1, 47.4 ppm. EIMS m/z ; $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$, [M] 316.

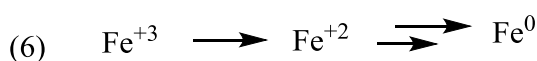
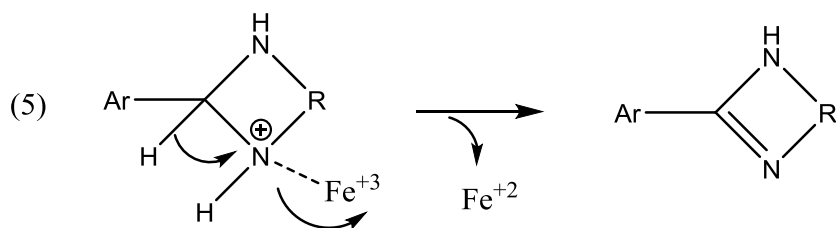
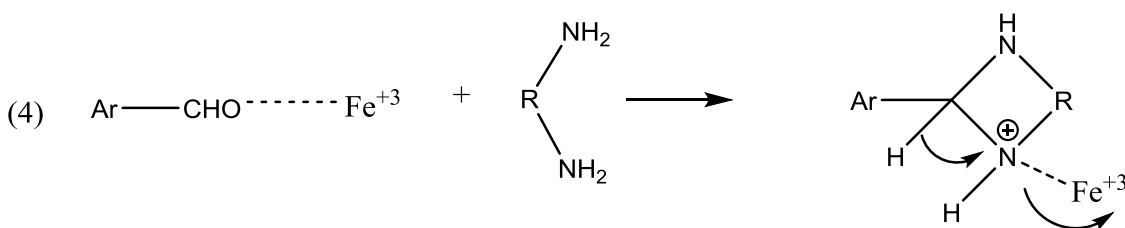
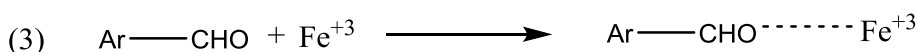
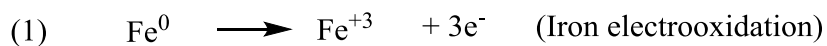
The morphology study of the iron wire, before and after the electrosynthesis, was done by SEM and EDS elemental analysis. Both samples were analyzed without any previous preparation. Figure 3 shows SEM images and allow to describe the effect of electrochemical Fe oxidation on the metallic wire. Table 2 shows wire EDS analysis before and after the induced electrolytic process (constant imposed potential of 0.65V/Ag/AgCl/Cl⁻_(MeOH)). As shown in Figure 3c, a change occurs in the wire surface since a larger amount of Fe appear. This fact implies that a new Fe phase was formed, as Fe₂O₃. The proposal is that formed oxide is the final state of iron after serving as catalyst on the benzimidazoles reaction.

Table 2. Elemental analysis from EDS of Fe electrode, before and after the synthetic process.

Element	Before electrochemical oxidation (Atomic %)	After electrochemical oxidation (Atomic %)
Fe	64.17	73.8
C	26.46	21.95
O	9.37	4.25

Results allow to propose that the synthetic process reached a metastable equilibrium on the electrode surface, since as soon as Fe appeared in the reaction medium, it is available as acid catalyst; however, reaction conditions may go until Fe₂O₃ crystals. Moreover, a plausible mechanism for the formation of benzimidazole derivatives by means of an assisted electrochemical catalyst formation is shown in Scheme 2. The oxidation of iron electrode occurs and produce a small amount of Fe⁺³ cation (step 1), which in basic conditions can be formed the iron oxide (step 2). Small amount of Fe⁺³ cation as a Lewis acid can activated the carbonyl group of the aldehyde (step 3) to increase the electrophilic character of the carbonyl groups and decrease the energy of the transition state [50]. This was followed by the attack of amino group from 1, 2 benzenediamine on the activated carbonyl group, resulting in the formation of diamine gem (step 4). The oxidation reaction of HC-NH bond is carried out by the

presence of Fe^{+3} cation (step 5). In fact, Fe_2O_3 (electrochemistry reaction) or FeCl_3 (Catalyst reaction) compounds are required for the formation of both the imine and the condensation process [51]. This reaction may reduce the ionic Fe(III) formed by oxidation process again to Fe^0 (step 6). However, kinetics certainly determine the reaction advance of Fe reduction that also have to compete with irreversibility of Fe surface change from Fe to Fe(III) and finally Fe_2O_3 species stabilize on the wire surface as showed in SEM analysis.



Scheme 2. Proposed mechanism for benzimidazoles synthesis.

4. CONCLUSION

A simple and no solid residues method for the synthesis of mono and di substituted benzimidazoles were performed. Supporting electrolyte composed by organic salts in MeOH played an important role in Fe electro-oxidation rate and the onset potential of bulk Fe dissolution. The reaction paths were through an acid catalysis induced by the presence of Fe(III) species on a pure Fe wire surface. The synthesis of 2-Aryl-1*H*-benzo[d]imidazole and 1-benzyl-2-aryl-1*H*-benzo[d]imidazole derivatives via the *in-situ* preparation of Fe(III) by an electrochemical process, was very efficient, safe and inexpensive, since catalyst was obtained under soft conditions reaction generating extremely small amounts of electrooxidized Fe ($\sim 3.50 \times 10^{-6}$ mol in half hour). SEM and optical microscopy analysis

corroborate that the final iron species was Fe₂O₃ on the Fe wire after its electrochemical oxidation. This method avoid excessive amounts of Fe(III) and do not require its subsequent removal, thus it demonstrate to be an innovative green procedure. Excellent results are obtained by the electrochemical production of Fe(III) catalyst in TBATFB/MeOH compared with the alumina-FeCl₃ (<15%) since at 0.5 h. the reaction proceeded at 90 and 99%, for mono and disubstituted benzimidazoles with a faster and more efficient process. The monosubstitued benzilimidazole (3OH-BZ-imidazole) showed its expected Fe corrosion inhibition by I vs. t plot traced at 0.65V/Ag/AgCl/Cl⁻_(sat MeOH). It is of interest to note that this procedure will find important applications in the synthesis of several condensation processes. Also it is of our interest to explore the iron surface reactions during the synthetic path.

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