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Article

Fast electrochemical method for organic dye decolorization using the recycled Li-ion batteries

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Abstract: In this paper the application of recycled Li-ion batteries spent cathode (LIB-SC) combined with $NaHCO_3/H_2O_2$ system is presented for the first time in the literature as an alternative for degradation of potentially toxic organic molecules. The model pollutant choice was methylene blue molecule. The spent cathode composition corresponds to $LiCoO_2$, which was proved by the XRD and EDX. Regarding the decolorization of methylene blue solution, the addition of $NaHCO_3$ in comparison with only H_2O_2 reduces the complete decolorization time in 96%. This reduction occurs because the radical $CO_3^{\cdot -}$ is more stable than OH. In this way, the application the system proposed in this article is aimed at solving two major global problems: the disposal of cell phone batteries and the pollution of liquid effluents.

Keywords: Recycling; Li-ion; methylene blue; $LiCoO_2$

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1. Introduction

One of the first papers reported about the Li-ion battery (LIB) is dated 1962 [1]. Until its insertion in the commercial market by Sony©, approximately 30 years passed. The LIB rapidly replaced the NiCd and NiMH batteries, generating a revolution in the production of electronic portable devices [2]. The LIB currently account for 37% of all batteries consumed in the world [3]. In order to have the dimension of LIB insertion in the market, in 2012 world sales of LIB was estimated at $12 billion and this number was more than double in 2015 ($30 billion) [4].

Due to the current needs for self-sustaining technologies, the recycling of Li-ion batteries (LIB) is a research topic that grows stronger with each passing year. In LIB the current density is generate by transport of Li^+ between the cathode (composed of intercalation oxides such as $LiCoO_2$ or $LiCo_xMn_yNi_wO_2$, with x+y+w =1) and the lithiated graphitic carbon anode [5]. The electrolyte is typically the $LiPF_6$ dissolved in organic carbonates [4]. The more abundant (around 25-30% in mass) and valuable component of LIB´s corresponds to the cathode [2]. In the literature there are a considerable amount of articles about the recycling of Li-ion batteries spent cathode (LIB/SC) composed by $LiCoO_2$. In laboratory scale, the first step of hydrometallurgical recycling is the cathode detachment of Al current collector followed by acid dissolution [5]. After dissolution, the metal cations are separated by application of a cationic resin [6]. Components such as Co and Li are recovered in form such as $Co(OH)_2$ e Li_2CO_3 or even the resynthesis of cathodic material is proposed [5]. Although there are many studies of LIB/SC recycling, very few studies point the direct application of LIB/SC [7].

The recent literature describes the decolorization of the methylene blue (MB) solution using the LIB/SC (with $LiCoO_2$) in presence of H_2O_2**[7]**. In this case the $OH^{\cdot}$ radical formation occurs through the $LiCoO_2$ delitiation promoted by hydrogen peroxide reduction of (Eq.2) **[7]**. The formation of hydroxyl radical ($OH^{\cdot}$) was confirmed by utilization of isopropanol (i-PrOH) as a scavenger **[7]**.

$$H_2O_{2(aq)} + e^- \rightarrow OH^{\cdot}_{(aq)} + OH^-_{(aq)} \qquad \text{(Eq.1)}$$

$$LiCoO_{2(s)} + \rightarrow Li_{(1-x)}CoO_{2(s)} + xLi^+_{(aq)} + xe^- \quad \text{(Eq.2)}$$

The literature shows that $NaHCO_3$ can increase the rate of methylene blue decolorization promoted by $OH^{\cdot}$ radicals. This is expected once the bicarbonate anion is radical scavenger (Eq.3) **[8].** The radical $CO_3^{\cdot}$ is much more stable than $OH^{\cdot}$, which can be explained by the difference in its recombination constant. For the radical $OH^{\cdot}$ the recombination constant is around $10^9 M^{-1}s^{-1}$ against $4.25x10^6 M^{-1}s^{-1}$ for the $CO_3^{\cdot -}$**[8]**.

$$OH^{\cdot}_{(aq)} + HCO^-_{3(aq)} \rightarrow H_2O + CO^{\cdot}_{3(aq)} \qquad k = 1.0x10^7 M^{-1}s^{-1} \text{(Eq.3)}$$

Thus, the objective of this paper is to study the methylene blue (model pollutant) decolorization using the Li-ion batteries spent cathode (LIB/SC) combined with $NaHCO_3/H_2O_2$ system. The composition of LIB/SC was obtained using the XDR and EDX techniques. An electrochemical study was also performed through linear voltammetry to evaluate the $OH^{\cdot}$ formation.

2. Material and Methods

2.1. Obtention and characterization of Li-ion batteries spent cathode (LIB/SC)

The Li-ion battery was manually dismantled and the spent cathode in tape form was separated. The cathode tape was heated at 200 ºC for 5h to remove organic solvents. The spent Li-ion battery cathode (LIB-SC) tape was wash in distilled water for eliminate the possible lithium salt (such as $LiPF_6$) presents in the electrolyte **[7]**. The crystalline structure of the spent Li-ion battery cathode tape was characterized by X-ray diffraction on a 200 B Rotaflex-Rigaku with Cu K_α irradiation, a Co filter, and scanning speed of 0.02º min^{-1}. The morphology of the spent Li-ion battery cathode tape was observed by Field-Emission Scanning Electron Microscopy on a JEOL JXA model 8900 RL equipped with an energy dispersive X-ray (EDX) detector.

2.2. Methylene blue decolorization analysis

To study the MB decolorization kinetic, a 100mL jacketed glass reactor containing 50 mL of MB solution were stirred magnetically (10 rpm) in a temperature controlled bath (25^{o}C). Before the H_2O_2 and $NaHCO_3$ addition, the MB solution was put in contact with LIB-SC for 2 hours to establish the adsorption equilibrium. The decolorization process was monitored analyzing aliquots at 659nm using a UV-Spectrophotometer FEMTO Cirrus 80 PR. All measurements were made in absence of visible light to avoid the possible electron excitation of cobalt lithium oxide conduction band to the valence band generating the electron (BC) and hole (BV) pair [7].

2.2. Linear voltammetry measurements

Linear voltammetry were made using an AUTOLAB PGSTAT 30 power supply. The working electrode was made of Li-ion batteries spent cathode (LIB/SC). The samples were prepared as rectangular pieces ($1cm^{-2}$). The auxiliary electrode, with an area of 3.75 cm^2, was made of platinum. A saturated Ag/AgCl reference electrode was used. All the electrochemical

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measurements were performed at 25 °C. After experiment the resultant solution was analyzed with AAS aiming to determine the possible lixiviation of Co and Li.

3. RESULTS AND DISCUSSION

3.1. Characterization of Li-ion batteries spent cathode (LIB-SC)

The characterization of Li-ion batteries spent cathode (LIB-SC) is very important since that its composition vary with the mark and even with model **[7]**. Figure 2 shows the X-ray diffraction of Li-ion batteries spent cathode (LIB-SC). According to comparison with the JCPDS card number 50-653, the main phase identified was in the $LiCoO_2$. The presence of graphite is justified because its addiction increase the cathode conductivity. Through SEM (Figure 3-a) it is possible to observe a very porous material which may contribute to the rapid reach of adsorption equilibrium. The porosity was calculated using the imagej© software and the value found was 42% and the average size of grain is $32 \mu m^2$. The presence of Fluor is due to binder polyvinylidene-fluoride (PVDF) (Figure 3-b) **[7].**

3.2. Decolorization of MB solution using LIB-SC + $H_2O_2/NaHCO_3$ system

Figure 4 shows the variation of $[MB]/[MB_0]$ vs. time (where the $[MB]_0$ are the initial MB concentration) using H_2O_2 and LIB-SC. From figure 4 it is clearly observed the great influence of LIB-SC in the MB decolorization reaction, as already described in the literature [7]. In this reaction, the H_2O_2 electrochemical reduction promoted by $LiCoO_2$ delitiation, is related with the first step [7]. The subsequent step is the attack of $OH^{\cdot}$ onto MB molecule. In the literature this step is commonly described as the reaction determinant step (rds) and depends of $OH^{\cdot}$ and MB concentrations [8]. Considering that, the electrochemical step maintains a practically fixed concentration of $OH^{\cdot}$, the more appropriate kinetic model is the pseudo first-order reaction as represented by Eq. 4 (where k_{app} is the apparent velocity constant) [8]. The detail in Figure 4 shows the linearity of $\ln[MB]/[MB]_0$ versus time as predicted for a first-order reaction (Eq.5).

$$\frac{d[MB]}{dt} = -k[OH^{\cdot}][MB] \approx -k_{app}[MB] \qquad \text{(Eq.4)}$$

$$\frac{[MB]}{[MB]_0} = \exp(-k_{app}t) \qquad \text{(Eq.5)}$$

Figure 5 shows the decolorization of MB solution using the H_2O_2 and the LIB spent cathode and HCO_3^-. Through Figure 5, one can see that the addition of HCO_3^- increased significantly the kinetics of MB decolorization once the bicarbonate anion is radical scavenger (Eq.3) **[8]**. Addition of $NaHCO_3$ reduces the time for complete decolorization from 150 to 6 minutes. Thus, to better understand the role of each component in the MB decolorization reaction, was made the variation of $[MB]_0$, $[HCO_3^-]$, $[H_2O_2]$ and LIB-SC area.

3.2.1. Variation of $[MB]_0$ and LIB-SC area in decolorization of MB using LIB-SC + $H_2O_2/NaHCO_3$ system

Figure 6 shows that the $[MB]_0$ variation promotes a modification in $[MB]/[MB]_0$ vs. time profile. However this behavior is not expected for a first order reaction (or pseudo first order reaction) since the $[MB]/[MB]_0$ vs. time curve must be an exponential curve that depends only of k_{app} such as shown in the Eq.5. The influence of dye initial concentration is reported in the literature for heterogeneous Fenton-like catalyst **[9]**. Considering that the adsorption equilibrium is reached quickly, initially the catalyst surface is saturated with MB molecules causing the reaction to initially follow zero order kinetics (Eq.6) **[9]**. Thus in the zero order kinetics the $[MB]/[MB]_0$ vs. time curve (represented in the Eq.7) has a $[MB]_0$ dependent angular coefficient

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($k_{app/zero}$). The linear fit in the early reaction instants reveal that the $k_{app/zero}$ changes from 0.32 to 0.10min^{-1} when the initial concentration of methylene blue changes from 12 to 6ppm respectively.

$$\frac{d[MB]}{dt} \approx -k_{app}[MB] \approx -k_{app/zero} \qquad \text{(Eq.6)}$$

$$\frac{[MB]}{[MB]_0} = 1 - \frac{k_{app}t}{[MB]_0} \qquad \text{(Eq.7)}$$

It is important to note that the Fe_3O_4 is a very popular catalyst for dye organic pollutants and other toxic substances due to its high efficiency as well as its magnetic separation from the reaction medium **[9]**. In the literature Fe_3O_4 nanoparticles are used for 10ppm MB degradation using only H_2O_2 (without the use of $NaHCO_3$)**[9]**. The time required for total decolorization was 120 minutes. In our work a solution of 12 ppm was completely discolored in 36min (0.5% of color – detail in the Figure 6).

Figure 7 shows the variation of LIB-SC area in the methylene blue decolorization process. Since hydroxyl radicals are formed by H_2O_2 and LIB-SC electrochemical reaction, it is natural that the LIB-SC area is directly proportional to the hydroxyl initial concentration. The linear fit in the early reaction instants reveal that the $k_{app/zero}$ reduce by a factor of 8 when the area undergoes a reduction of 16cm^2 to 2cm^2.

3.2.2. Variation of $[H_2O_2]_0$ and $[NaHCO_3]_0$ in Decolorization of MB using LIB-SC + $H_2O_2/NaHCO_3$ system

Figure 8-a and 8-b shows the variation of $NaHCO_3$ and H_2O_2 concentration in MB decolorization respectively. It would be expected that with increasing in $NaHCO_3$ concentration there would be an increase in $CO_3^{\cdot-}$ concentration, which would lead to an increase in the MB decolorization rate. However, what is observed is that with $NaHCO_3$ increase from 0.01 to 0.03molL^{-1}, there is a subtle decrease in the MB decolorization rate. This effect is probably linked to the recombination of $CO_3^{\cdot-}$ radicals as shown in Eq.3.

The increase in peroxide concentration has a negligenciable influence on the reaction rate of MB decolorization (Figure 8-b). On the other hand, the peroxide concentration should influence the reaction rate since it is a reagent of the electrochemical step as shown in Eq.1. However peroxide is also a scavenger of $OH^{\cdot}$ radicals producing hydroperoxyl radicals ($HO_2^{\cdot}$).

$$OH^{\cdot}_{(aq)} + H_2O_{2(aq)} \rightarrow H_2O + HO^{\cdot}_{2(aq)} \qquad k = 3.3x10^7 M^{-1}s^{-1} \qquad \text{(Eq. 8)}$$

As described in the literature, the $HO_2^{\cdot}$ generated in Eq. [10] contributes very little to the process of organic molecules degradation **[10].**

3.3. *Linear polarization analyses and Co and Li lixiviation*

In order to better investigate the electrochemical step of MB decolorization, figure 9 shows the linear voltammetry of LIB-SC (area = 1cm^{-2}) in a solution with MB and $H_2O_2/NaHCO_3$ system. The table 1 shows some parameters obtained from linear voltammetry (figure 9). The anodic branch refers to $LiCoO_2$ delitiation (eq. X) and the cathodic branch corresponds to the reduction of H_2O_2 (Eq.2). Considering the one electron charge transfer process as the limiting step, the Tafel coefficient must be near 118mV/dec. In this work the deviations of this value can be attributed to an asymmetry in the charge transfer barrier that can be caused by adsorption of MB **[7]**. The equilibrium potential (E) found is within that expected for the $LiCoO_2$ in aqueous medium **[11]**. Considering the one electron transfer (n=1), the exchange current (i) as 19x10^{-2}Am^{-2}, the reaction system volume (V) as 5x10^{-2}L and F (Faraday constant) equal to 96500Cmol^{-1}, we can use Faraday's law (Eq.9) to obtain the production rate of Li^+ ions in solution.

$$\frac{d[Li^+]}{dt} = \frac{i}{VnF} \qquad (Eq.9)$$

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The value found was 4 x 10^{-4} $molm^{-3}s^{-1}$ (in the SI) or 4 x $10^{-8}Ms^{-1}$. Thus, at the end of 5 min we should have a Li ($7gmol^{-1}$) concentration around 0.084ppm. Figure 10 shows the determination of lithium and cobalt after 5 and 60min of reaction. The time of 5 min was chosen because this is the time interval necessary to degrade 6 ppm of methylene blue. It is observed that for the complete decolorization of the solution (approximately 5min) the cobalt leaching is below 0.015ppm and lithium this value corresponds to 0.055ppm. Despite the high efficiency a disadvantage of the method is the leaching of Li and Co into the reaction medium.

3. Conclusion

In this work the application of recycled Li-ion batteries spent cathode (LIB-SC) combined with $NaHCO_3/H_2O_2$ system is presented for the first time in the literature as an alternative for the degradation of potentially toxic organic molecules. The model pollutant choice was methylene blue molecule. The studied cathode has the composition $LiCoO_2$. The porosity was calculated and the value found was 42% and the average size of grain is 32µm². Regarding the decolorization of methylene blue solution, the addition of $NaHCO_3$ reduces the time for complete decolorization from 150 to 6 minutes. This reduction in time occurs due to more stable CO_3 radical is much more stable than OH·. In this way, the application the system proposed in this article is aimed at solving two major global problems: the disposal of cell phone batteries and the pollution of liquid effluents.

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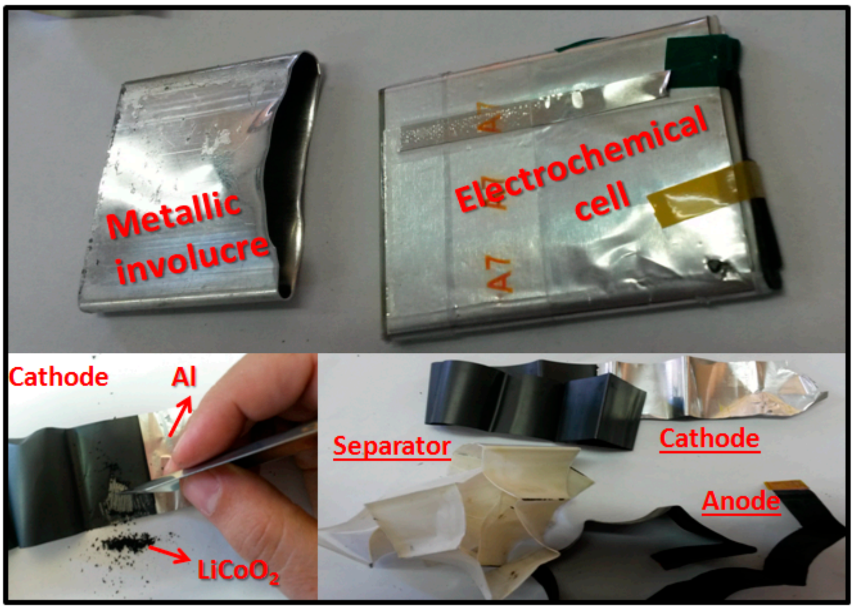


Figure 1 – Dismantling scheme and obtaining of Li-ion batteries spent cathode (LIB/SC).

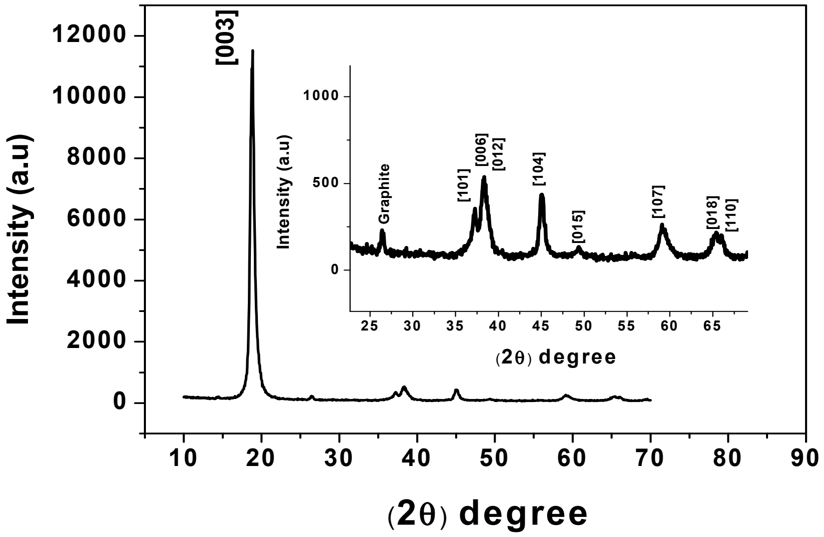
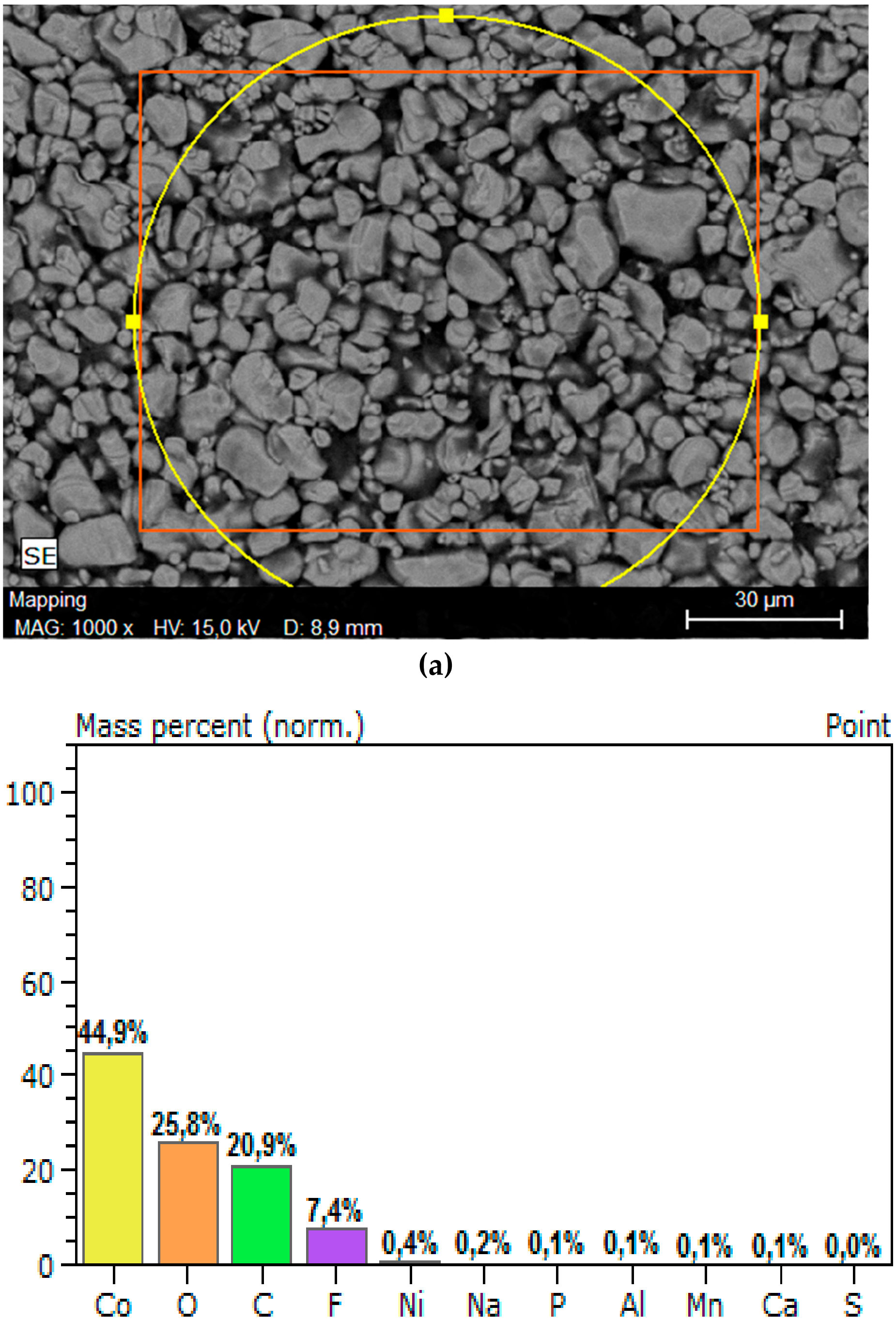


Figure 2 – X-ray diffraction of Li-ion batteries spent cathode (LIB/SC) after heating at 200 ºC for 5h.



(a)

(b)

Figure 3 –Scan electronic microscopy (SEM) and the average chemical composition obtained of energy dispersive X-ray (EDX) analyses of LIB/SC after heating at 200 ºC for 5h.

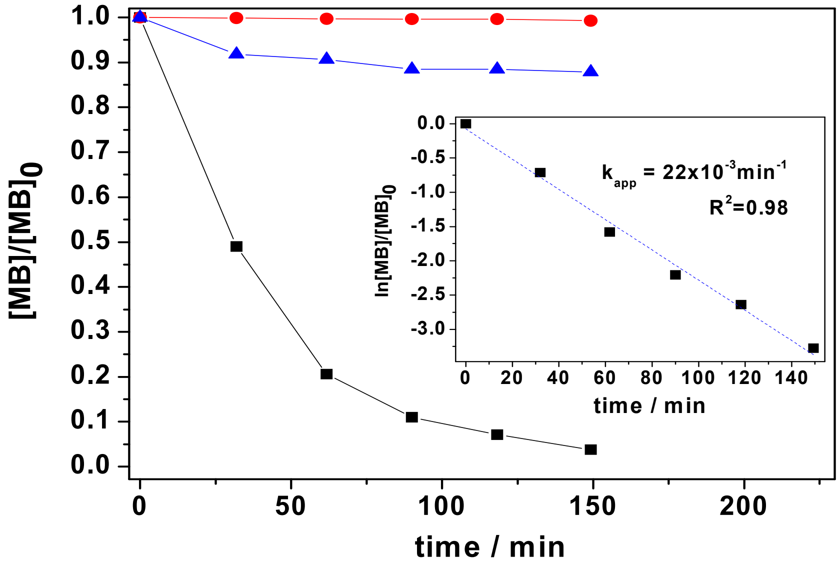


Figure 4 – Decolorization of MB solution in different conditions. Only [MB] = 6ppm (red). [MB] = 6ppm + [H_2O_2]= 0.03M (blue). With LIB-SC (area = 16cm^{-2} ~400mg) + [MB] = 6ppm + [H_2O_2]= 0.03M (black).

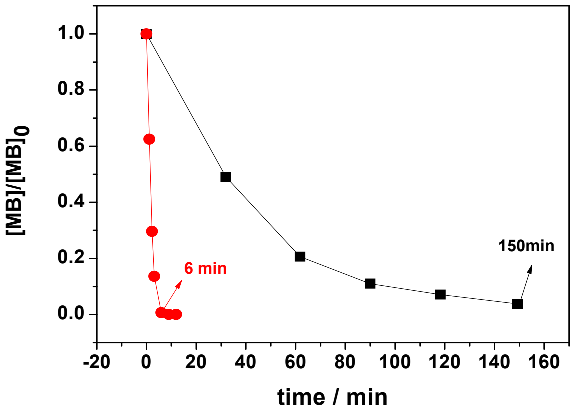


Figure 5– Decolorization of MB solution in different conditions: [MB] = 6ppm + H_2O_2 = 0.03M + LIB spent cathode tape (area = 16cm^{-2}) (Black). [MB] = 6ppm + H_2O_2 = 0.03M + LIB-SC (area = 16cm^{-2}) + $NaHCO_3$ 0.01M (red).

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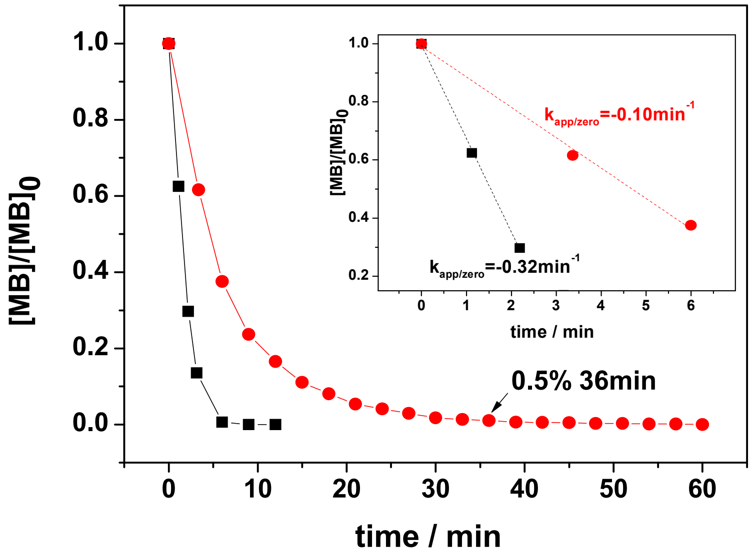


Figure 6– Decolorization of MB solution with two different $[MB]_0$: 6ppm (black) and 12ppm (red). In both cases was used $[H_2O_2] = 0.03M$ + LIB-SC (area = 16cm^{-2}) + $NaHCO_3$ 0.01M.

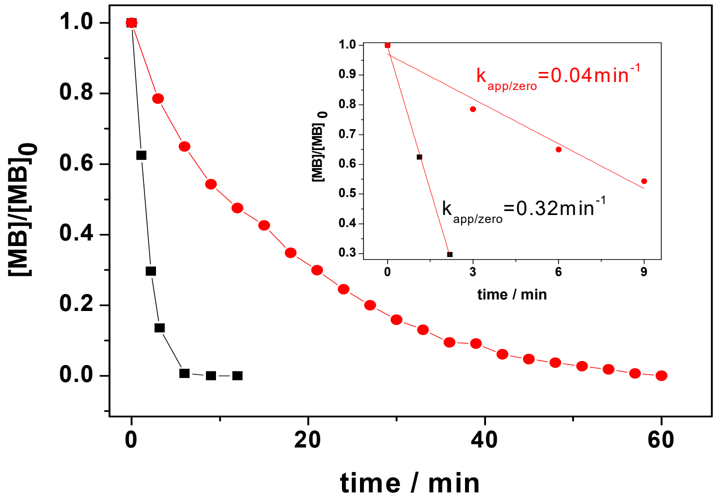
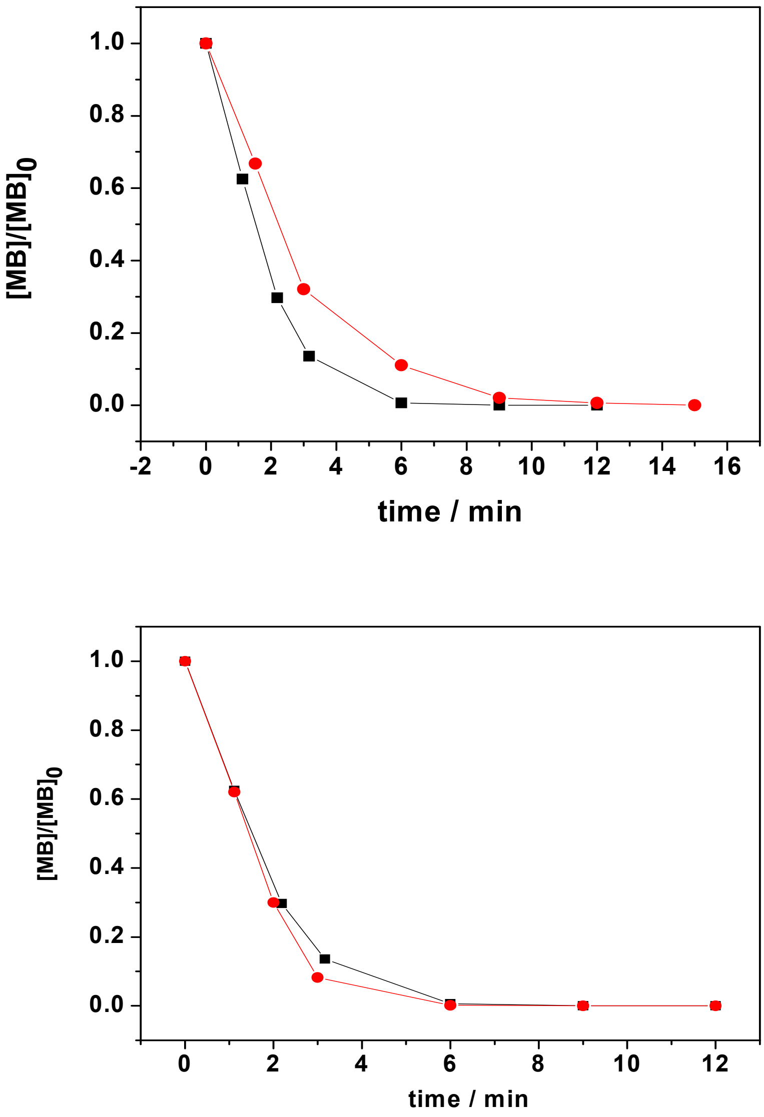


Figure 7– Decolorization of MB solution with two different LIB-SC area: 16 cm^{-2} (black) and 1cm^{-2} (red). In both cases was used [MB] = 6ppm + H_2O_2 = 0.03M + LIB spent cathode tape (area = 16cm^{-2}+ $NaHCO_3$ 0.01M.



(a)

(b)

Figure 8– (a) Decolorization of MB solution with two different $[NaHCO_3]_0$: (black) 0.01 and 0.03 (red). In both cases was used $[H_2O_2] = 0.03M$ + LIB-SC (area = 16cm^{-2}) + [MB] = 6ppm. (b) Decolorization of MB solution with two different $[H_2O_2]_0$: (black) 0.03 and 0.01 (red) In both cases was used $[NaHCO_3]=0.01M$ + LIB-SC (area = 16cm^{-2}) + [MB] = 6ppm.

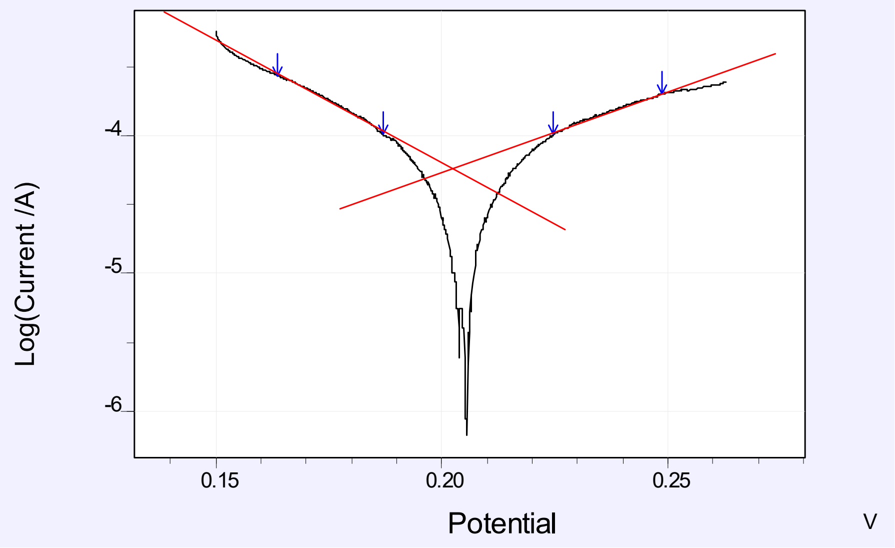


Figure 9 Linear voltammetry of LIB-SC (area = 1cm^{-2}) in a solution with MB and $H_2O_2/NaHCO_3$ system (scan rate = 1mVs^{-1}).

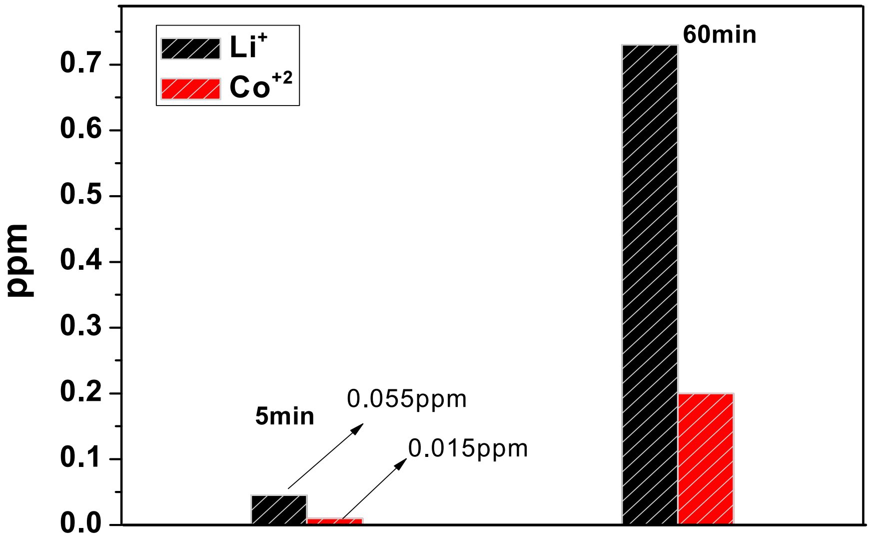


Figure 10– Lithium and cobalt detection using AAS after the discoloration of MB solution using: [MB] = 6ppm + H_2O_2 = 0.03M + LIB spent cathode tape (area = 16cm^{-2}) + $NaHCO_3$ 0.01M.

Table 1 - Some parameters obtained from linear voltammetry of LIB-SC (area = 1cm^{-2}) in a solution with MB and H_2O_2/$NaHCO_3$ system.

Parameter	**Value**
E	202.4 mV
i	56.46 μAcm^{-2}
b_a Vdec^{-1}	0.152
b_c Vdec^{-1}	0.096