

Original Research Article

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ELECTROCHEMICAL STUDY OF ALBENDAZOLE AND MEBENDAZOLE ADSORBATES ON ACTIVATED CHARCOAL MODIFIED ELECTRODE

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ABSTRACT: Benzimidazoles are bioactive compounds which display a wide range of therapeutic activities. Although greatly metabolized by first pass effect when drug use is concerned, benzimidazole presence in industrial wastewater and soil is a common occurrence, which lifts concerns about their environmental hazards. Since activated charcoal (Ac) adsorption is a widely used method for pollutants remediation, information regarding adsorption processes in both disperse matrixes and adsorbant surface may be noteworthy to provide a better understanding on drug removal dynamics. The aim of this work was therefore, to provide the first report regarding the voltammetrical study of benzoimidazole adsorbates, namely Albendazole (AL) and Mebendazole (MB), on Ac dispersions and Ac modified electrode surface. AL and MB were assessed in liquid and solid phase by differential pulse voltammetry using Ac modified electrode. The results showed that AL overall concentration in liquid media was almost akin to that of solid phase, whereas for MB, adsorbate concentration was significantly higher than in solution, which is justified by MB chemical structure. These findings indicate that AcCPE may be a viable option to study benzimidazole adsorbates.

KEYWORDS: adsorbates; voltammetry; activated charcoal; modified electrode.

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1. INTRODUCTION

Benzimidazoles are bioactive compounds which display a wide range of therapeutic activities. Amongst their main representatives are drugs such as albendazole (AL) and mebendazole (MB), whose anti-parasitical proprieties turn them into widely used medicines in developing countries. Hence high demand, benzoimidazole production is a thriving field, which lifts concerns about their potential environmental impacts [1-2-3]. Although greatly metabolized by first pass effect when drug use is concerned, benzimidazole presence in industrial wastewater and soil is a common occurrence. Since such compounds exhibit high stability and are prone to interact with non-targeted ecological receptors, their remediation in both urban and industrial effluents is of utmost importance [4-5-6]. Amongst the different methods employed for wastewater contaminants remediation, adsorption processes are valuable due to their low cost and practicality. Moreover, these methods are versatile, as a plethora of different adsorptive matrixes can be employed in order to reach an optimal remediation level. Some matrixes such as activated charcoal (Ac) are capable of electric conduction, which henceforth allows the use of electrochemical methods as voltammetry to determine adsorbate concentration instead of only liquid phase assessment [6-7-8]. Voltammetry is unique for drug and contaminant studies, due to the high selectivity displayed by this method towards electroactive analytes determination. Nonetheless, sensitivity can be further improved through the use of different electrode matrixes. Ac electrodes are valuable hence their adsorptive proprieties, which can be used to provide data from both adsorbates in solid phase and bulk fluid phase. This concomitant detection allows better inferences towards mass transfer processes [9-10-11]. Since information regarding adsorption processes in both disperse matrixes and electrode surface is noteworthy to provide a better understanding on drug removal dynamics, the aim of this work is to provide the first report regarding the voltammetrical study of benzoimidazole adsorbates, namely AL and MB, on Ac dispersions and Ac modified electrode surface.

2. MATERIALS AND METHODS

Samples and Reagents

All electrolyte salts, solvents and reagents were of analytical grade. Ac, graphite powder and mineral oil were purchased from Sigma Chemical Co. (St. Louis, MO, USA). Electrolyte solutions were prepared with double distilled Milli-Q water (conductivity $\leq 0.1 \mu\text{S cm}^{-1}$) Millipore S. A., Molsheim, France. AL and MB were donated by Pharmacy School Drugstore of Federal University of Goias, Goiânia-GO, Brazil. All standard solutions were prepared to render 1 mM stock solutions.

Electrode Preparation

In order to conduct voltammetric assays, an Ac carbon paste electrode (AcCPE) was constructed. Therefore, 90 mg of unmodified graphite powder was mixed with 10 mg Ac and 30 mg mineral oil, herein used as agglutinating agent. A carbon paste electrode (CPE) was made in order to serve as

control. CPE production process was undergone by mixing 100 mg of unmodified graphite powder with 30 mg of mineral oil.

Voltammetric Assays

Voltammetric experiments were carried out in a potentiostat/galvanostat Autolab III[®] integrated to the GPES 4.9[®] software, Eco-Chemie, Utrecht, Netherlands. The measurements were performed in a 1.0 mL one-compartment/three-electrode system electrochemical cell consisting of either CPE or AcCPE both 3 mm diameter, a Pt wire and Ag/AgCl/KCl_{sat} electrode (Lab solutions, São Paulo, Brazil), representing the working electrode, the counter electrode and the reference electrode, respectively. The experimental conditions for Differential Pulse Voltammetry (DPV) were: pulse amplitude 50 mV, pulse width 0.5 s, scan rate 10 mV.s⁻¹ and scan range of 0 to +1.0 V. The voltammetric assays were performed in 0.1 M phosphate buffer solution (PBS), at pH 7.0. DP voltammograms were background-subtracted and baseline-corrected to provide better data visualization, and all data was analyzed and treated with Origin 9[®] software.

Adsorption Study of AL and MB in Ac Aqueous Suspension

In order to better understand AL and MB adsorption on Ac aqueous suspension, an adsorption assay was conducted. The test was based in the preparation of 5 treatment solutions for each drug, namely t₀, t₁₅, t₃₀, t₆₀ and t₁₂₀. Each treatment solution corresponded to a specific time in minutes in which 10 mg Ac was suspended and left to adsorb the analyte. The solution was composed by 10 mL of PBS pH 7.0 and 50 µL of either AL or MB stock solutions (1 mM), leading to a final concentration of 5 µM. The final solid phase/ bulk fluid phase proportion for all experiments was 1:1 (w/v). To determine the concentration of each analyte adsorbed on Ac or present in bulk fluid phase, tests concerning solution and solid phase analysis were performed. After each given times, the solutions were filtrated in qualitative filter paper (Unifil, São Paulo, Brazil) and 1 mL of each filtrated was analyzed by DPV using AcCPE. The solid phase composed by analytes adsorbed on Ac was left to dry for 4 hours at 25 ± 2°C, and then, 5 mg of this material was employed to produce AcCPE with 15 mg unmodified graphite powder and 5 mg mineral oil. This analyte containing electrode was then used to determine adsorbates concentration through DPV on 1 mL electrochemical cell filled with PBS solution pH 7.0.

Adsorption Study of AL and MB in AcCPE surface

To comprehend AL and MB mass transfer processes on both CPE and AcCPE surfaces, an electrode surface adsorption assay was conducted. The test was based in the preparation of 5 treatment solutions for each drug, namely t₀, t₁₅, t₃₀, t₆₀ and t₁₂₀. Each treatment solution corresponded to a specific time in minutes in which the electrodes were immersed in solution, and left to adsorb the analyte. The solution was composed by 10 mL of PBS pH 7.0 and either AL or MB enough to a final concentration of 1 mM. After each given time, the analyte containing electrode was left to dry for

15 minutes, and then used to determine electrode surface adsorbates concentration through DPV on 1 mL PBS pH 7.0 electrochemical cell.

3. RESULTS AND DISCUSSION

Adsorption Study of AL and MB in Ac Aqueous Suspension

Compounds adsorption in matrixes such as Ac is a complex phenomenon, hence factors regarding analyte chemical structure, concentration, mass transfer processes and available bonding sites in adsorbent may interfere mid analysis, henceforth relative percentages concerning original concentration may not fit accordingly to removal rates [12-13-14]. For first assay, standard curves concerning AL and MB were performed (Figure 1. A, B, C and D), and AL and MB relative percentages concerning fluid phase original concentration were compared (5 μM) (Figure 2.A and B).

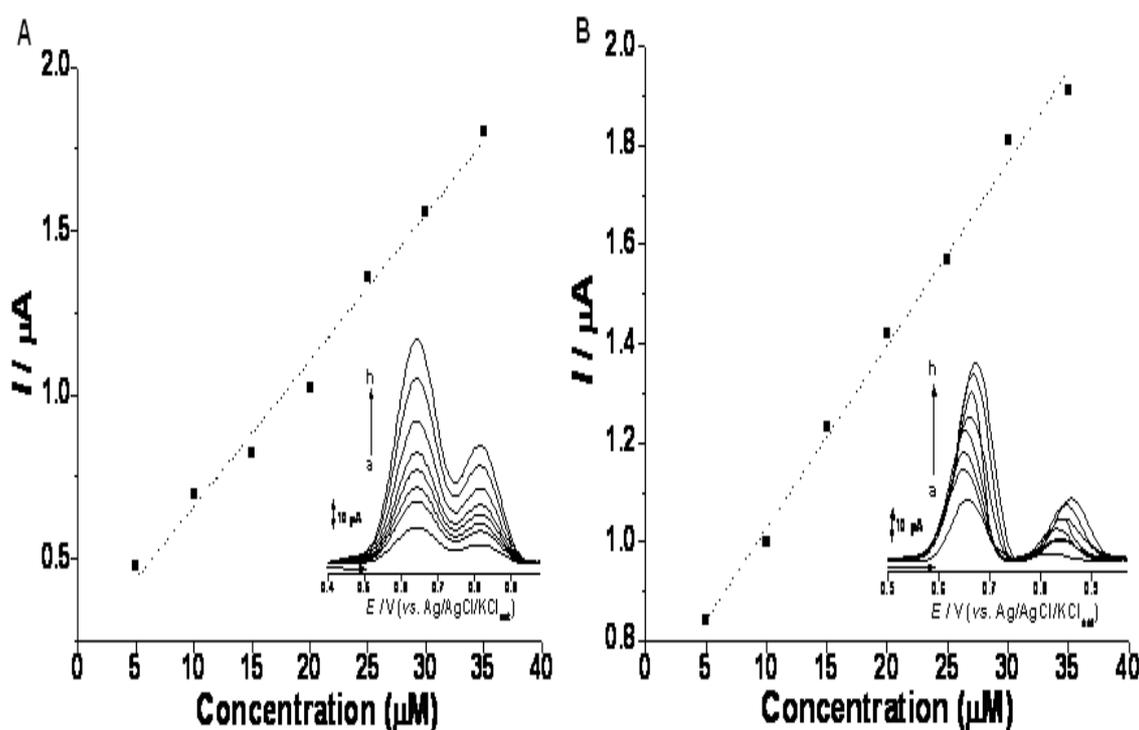


Figure 1.A. Standard curve of Albendazole ($r^2 = 0.990$) through DPV. **Insert.** DP voltammograms of Albendazole solutions (a \rightarrow h) at following concentrations: 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35 μM . **B.** Standard curve of Mebendazole ($r^2 = 0.984$) through DPV. **Insert.** DP voltammograms of Mebendazole solutions (a \rightarrow h) at following concentrations: 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35 μM Pulse amplitude 50 mV, pulse width 0.5 s and scan rate 10 mVs^{-1} . All analysis carried out in 0.1 M PBS, pH 7.0 at AcCPE.

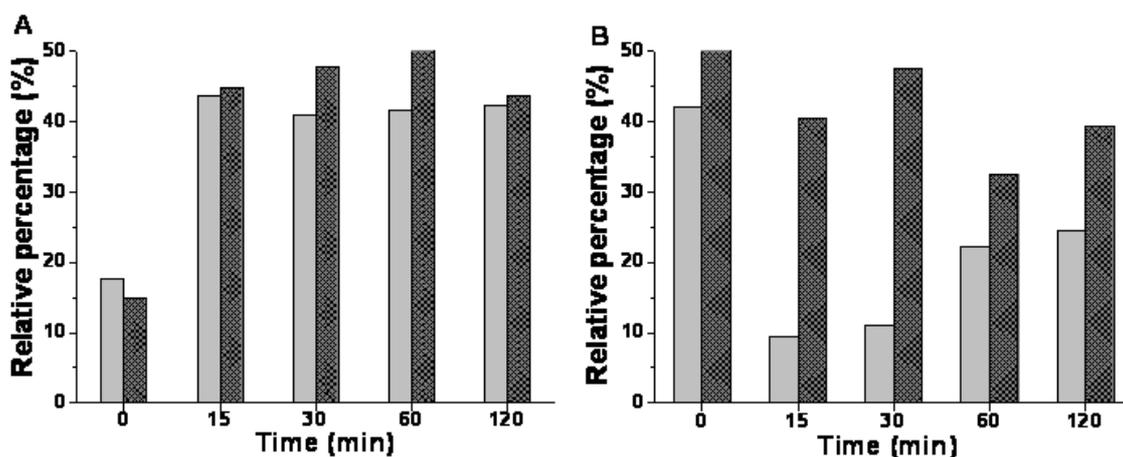


Figure 2.A. Depiction of AL detected in solution (light grey) and in activated charcoal (dark grey) at given times. **B.** Depiction of MB detected in solution (light grey) and in activated charcoal (dark grey) at given times.

The results showed that AL overall concentration in liquid media was almost akin to that of solid phase, whereas for MB, adsorbate concentration was significantly higher than in solution. These findings suggest therefore higher affinity between MB and solid phase, which can be attributed to MB molecules interaction with Ac [15-16-17]. Moreover, AL concentrations in solution presented little change from t15 to t120, hence suggesting Ac bonding sites saturation (Figure 2.A). Such trend was not followed on MB, whose concentrations in solution rose in the same interval, thus implying mass transfer processes on available bonding sites (Figure 2.B) [18-19-20].

Adsorption Study of AL and MB in AcCPE surface

Adsorption is greatly influenced by contact surface and adsorbent matrix constitution, which therefore implicates that, different electrode matrixes may display distinct adsorption profiles. Thus, an adsorption study was conducted to evaluate AL and MB interaction with electrode matrix surface (Figure 3.A and B).

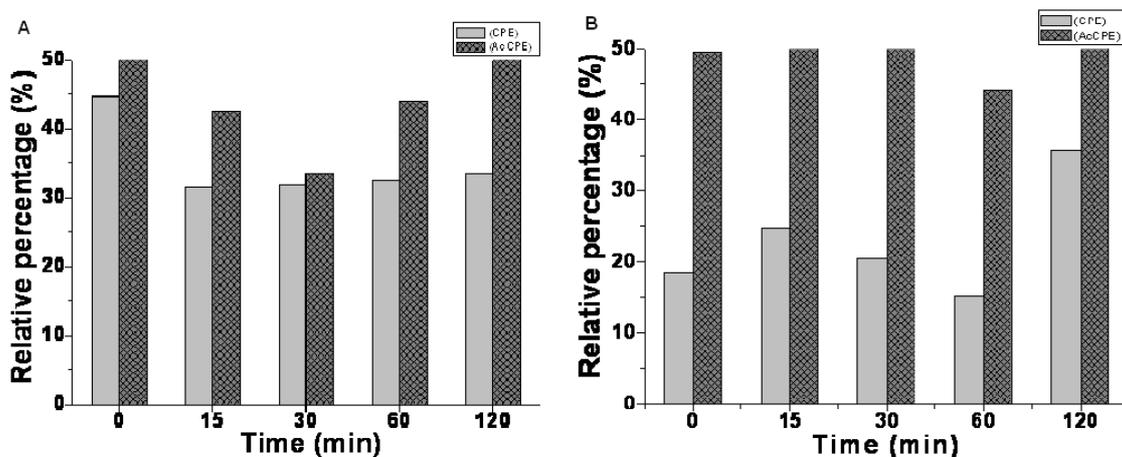


Figure 3.A. Depiction of Albendazole adsorbates detected in CPE and AcCPE at given immersion times in 0.1mM Albendazole solution. **B.** Depiction of Mebendazole adsorbates detected in CPE

and AcCPE at given immersion times in 0.1mM Mebendazole solution. Pulse amplitude 50 mV, pulse width 0.5 s and scan rate 10 mVs⁻¹. All analysis carried out in 0.1 M PBS, pH 7.0 at CPE and AcCPE.

Results indicate clearly that MB exhibits higher affinity towards electrode matrix (Figure 3.B). These findings are in consonance with literature hence MB chemical structure presents a terminal aromatic core prone to be adsorbed on carbon containing matrixes [21-22-23]. Although AL and MB structures are pretty similar due to the presence of the same pharmacophore, the presence of a terminal aliphatic chain in AL structure may hinder adsorption, thus culminating in the profiles seen. Furthermore, it can be hinted that activated charcoal removal may be a viable option to promote the remediation of benzimidazoles [24-25].

4. CONCLUSION

It is well reported in literature that Ac containing matrixes may display different removal isotherms according to system physicochemical features and compounds chemical structures. Therefore, the trends herein exhibited by both AL and MB are in consonance with literature. Moreover, MB presented higher affinity towards Ac matrix, hence its terminal aromatic moiety. Results indicate that AcCPE may be a viable option to study benzimidazole adsorbates.

5. CONFLICT OF INTEREST

Authors declare no conflict of interest.

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