#### Accepted Manuscript

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PII:	\$1572-6657(17)30802-0
DOI:	doi:10.1016/j.jelechem.2017.11.024
Reference:	JEAC 3654
To appear in:	Journal of Electroanalytical Chemistry
Received date:	3 June 2017
Revised date:	7 November 2017
Accepted date:	7 November 2017

Please cite this article as: F. Laghrib, W. Boumya, S. Lahrich, A. Farahi, A. El Haimouti, M.A. El Mhammedi , Electrochemical evaluation of catalytic effect of silver in reducing 4-nitroaniline: Analytical application. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Jeac(2017), doi:10.1016/j.jelechem.2017.11.024

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## **ACCEPTED MANUSCRIPT**

### Electrochemical evaluation of catalytic effect of silver in reducing 4-nitroaniline: Analytical application

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#### Abstract

The present work reports on electrocatalytic activity of silver electrode for 4-nitroaniline (4-NA) reduction, where its performance is compared with conventionally used electrodes (gold, graphite and glassy carbon). The voltammetric behavior of 4-nitroaniline (4-NA) is explored where a sensitive cathodic peak has appeared at about -0.26 V (vs. Ag/AgCl/3M KCl) in Britton Robinson buffer solution (pH 2.0). This peak results from the irreversible reduction of 4-NA at metallic silver electrode. The catalytic effect was evaluated using cyclic voltammetry and chronoamperometry. Indeed, the cathodic transfer coefficient was 0.57 and electron transfer rate constant was evaluated to be  $7.38 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>. Electrochemical impedance spectroscopy also confirms our experimental results as the silver electrode shows least charge transfer resistance. In order to provide electrochemical detection to reducing the nitro groups of 4-NA on the silver electrode surface, the differential pulse voltammograms were used in the potential range between 0.2 V and -1 V vs. Ag/AgCl/(sat. KCl).

Furthermore, silver electrode can be used successfully to improve the detection of 4-NA at very low concentration levels with high sensitivity. The linear calibration range was from  $8.0 \times 10^{-9}$  to  $1.0 \times 10^{-3}$  mol L<sup>-1</sup>. The limit of detection (LOD) was found to be  $4.74 \times 10^{-9}$  mol L<sup>-1</sup>, while relative standard deviation (RSD) at  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> 4-NA concentration was 1.94 %

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