

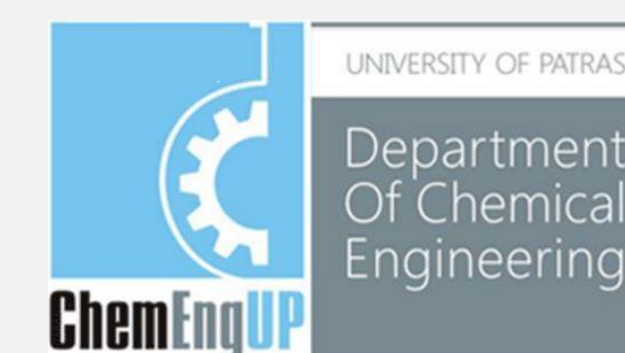
Electrochemical Mineralization of Antihypertensive Drug Valsartan for Wastewater Treatment



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Introduction

Aim of the study

The goal of this work was to explore for the first time the ability of boron-doped diamond electrochemical oxidation (EO) to degrade *valsartan* (VAL) at environmentally relevant matrices. Therefore, the efficiency of a) current density, b) VAL concentration, c) initial pH, d) supporting electrolyte, and e) water matrix were systematically investigated.

Background

Valsartan (VAL), is an effective Angiotensin II receptor blocker for the treatment of hypertension and heart attacks [1,2]. VAL belongs to the antihypertensive drugs group and is one of the most commonly consumed pharmaceuticals in the world, as it is highly effective compared to modern β -blockers [1,2]. In recent years, *advanced oxidations processes* (AOPs) have been widely tested against these persistent contaminants [3,4]. Among AOPs, the EO process, based on the situ formation of hydroxyl radicals generated directly by oxidation of water, has attracted scientific attention as a remediation technology for the treatment of organic contaminants from wastewater [5,6]. However, to the best of our knowledge, up to now, no research data are available about the EO treatment of VAL for its efficient removal in aqueous media.

Study Protocol

Experimental reactor set-up

Electrochemical experiments were conducted in batch mode using a plexiglass reactor with a working volume of 150 mL, open to the atmosphere at room temperature and without it being controlled. A thin film of BDD electrode with an active area of 8 cm² (Adamant Technologies SA, Switzerland; B/C 1000 ppm) was used as the anode, while a stainless steel plate (304 SS, active area 8 cm²) served as the cathode. The inter-electrode distance was about 9 cm.

Analysis

An HPLC system (Waters Alliance 2695) was used for the determination of VAL equipped with a diode array detector (Waters 2996). The stationary phase was a reversed-phase Kinetex C18 column, 150mm×3 mm, i.d. 2.6 μ m, purchased from Waters (Milford, MA, USA). The mobile phase consisted of ACN and 0.1% H₃PO₄, using an isocratic elution program. The flow rate was 200 μ L/min and the overall analysis time was 8 min. DAD was set at 230 nm.

Results

Representative results regarding the influence of various operating conditions on VAL oxidation are shown in figures 1-2. These experiments were performed containing 500 μ g/L VAL and 100 mmol/L Na₂SO₄ as supporting electrolyte in ultrapure water (UPW). VAL degradation in all reaction conditions followed the pseudo-first-order kinetic model.

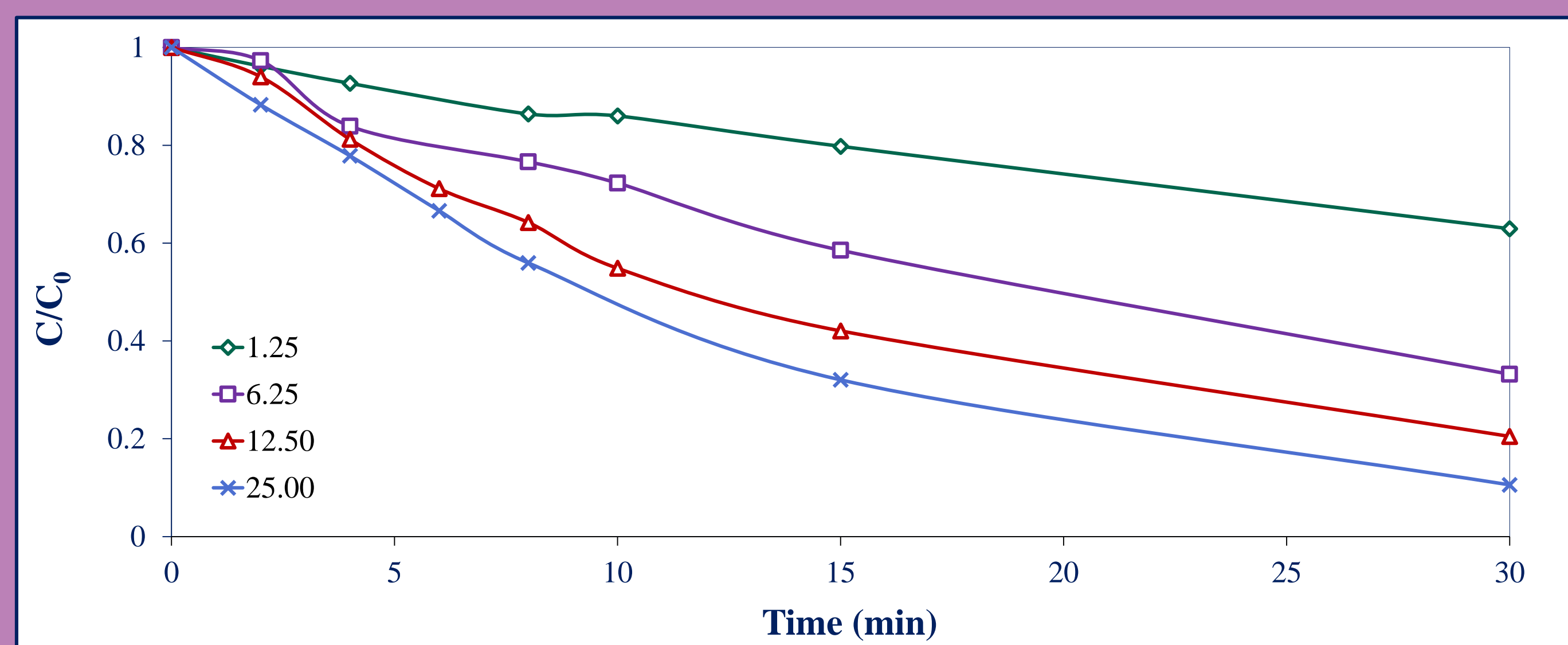


Figure 1. Influence of current density (J) in mA/cm².

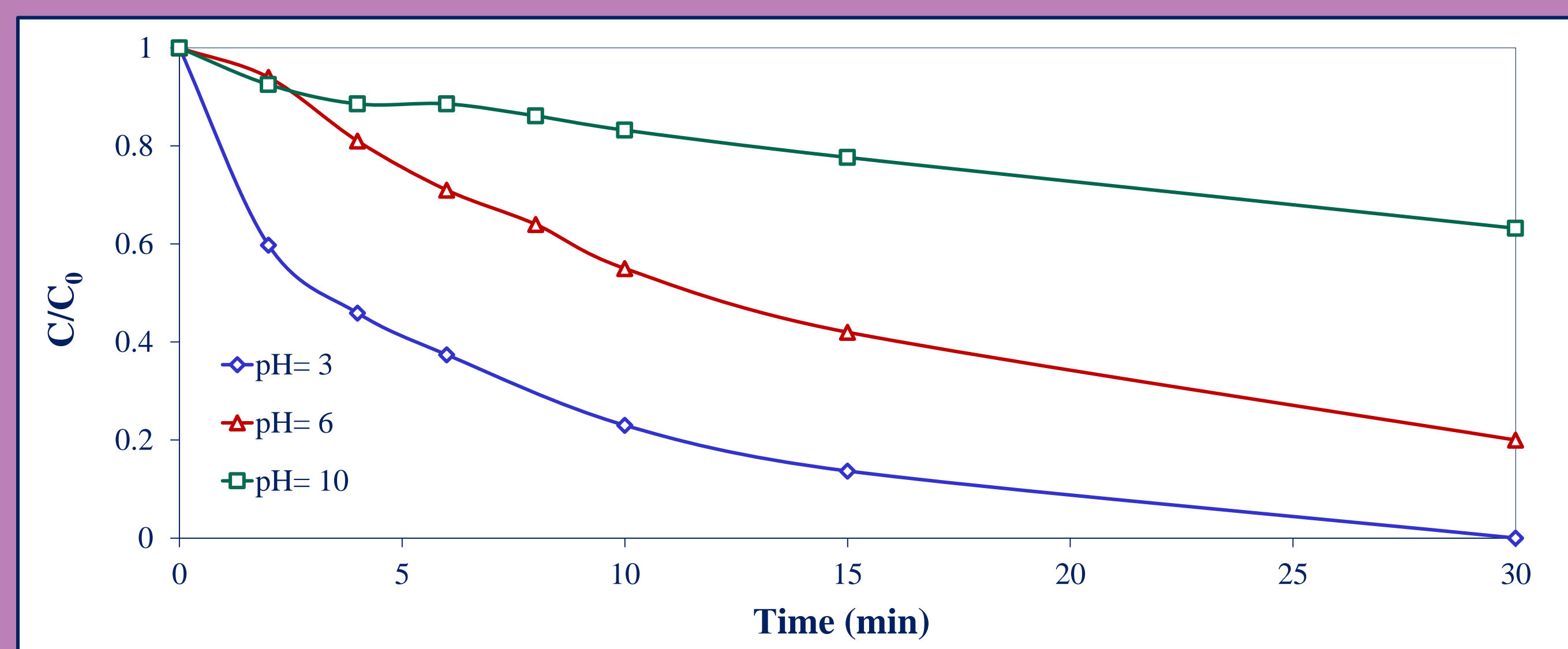


Figure 2. Influence of initial pH.

Experiments in actual water matrices (bottled water; BW and wastewater; WW), as well as in UPW spiked with 10 mg/L humic acid (HA) or 250 mg/L bicarbonate ions (BIC) or 250 mg/L chloride ions (Cl⁻) in the form of NaCl were carried out at 12.5 mA/cm² and 100 mmol/L Na₂SO₄, and contained 500 μ g/L VAL. Results are shown in figures 3-4 after 45min electrolysis time.

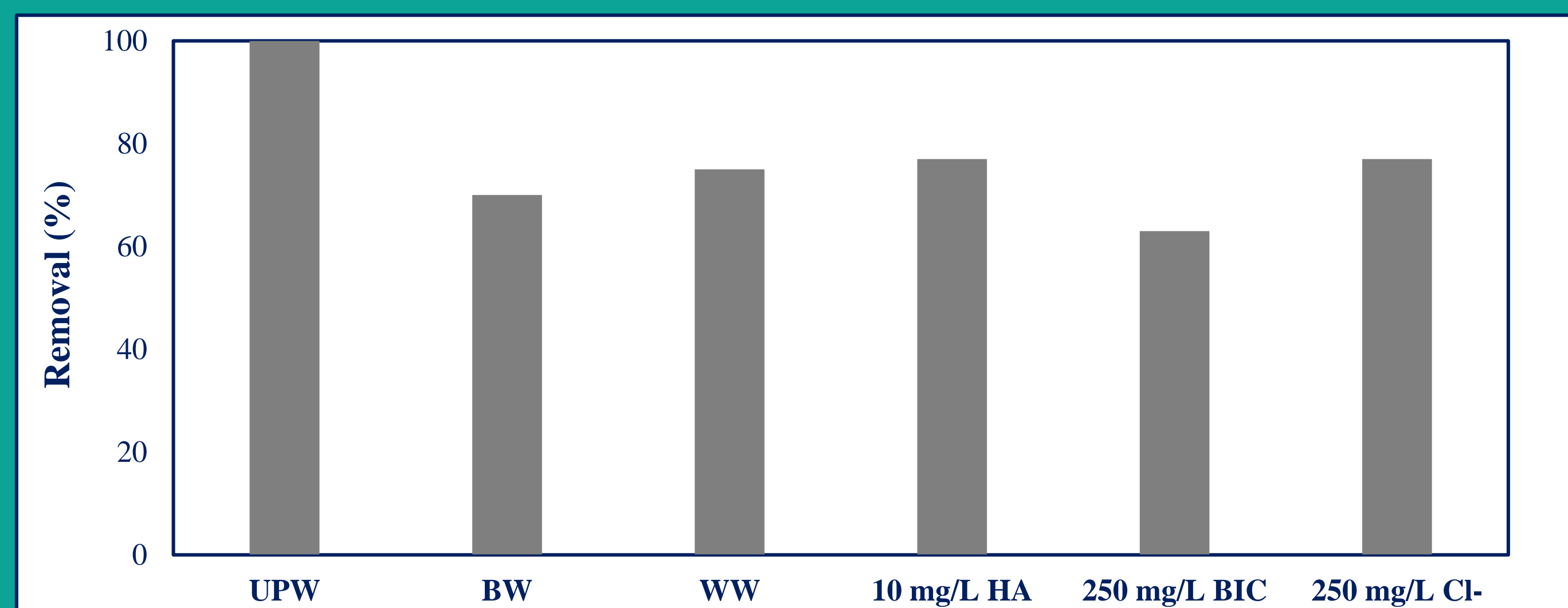


Figure 3. Percentage removal of water matrices and water constituents.

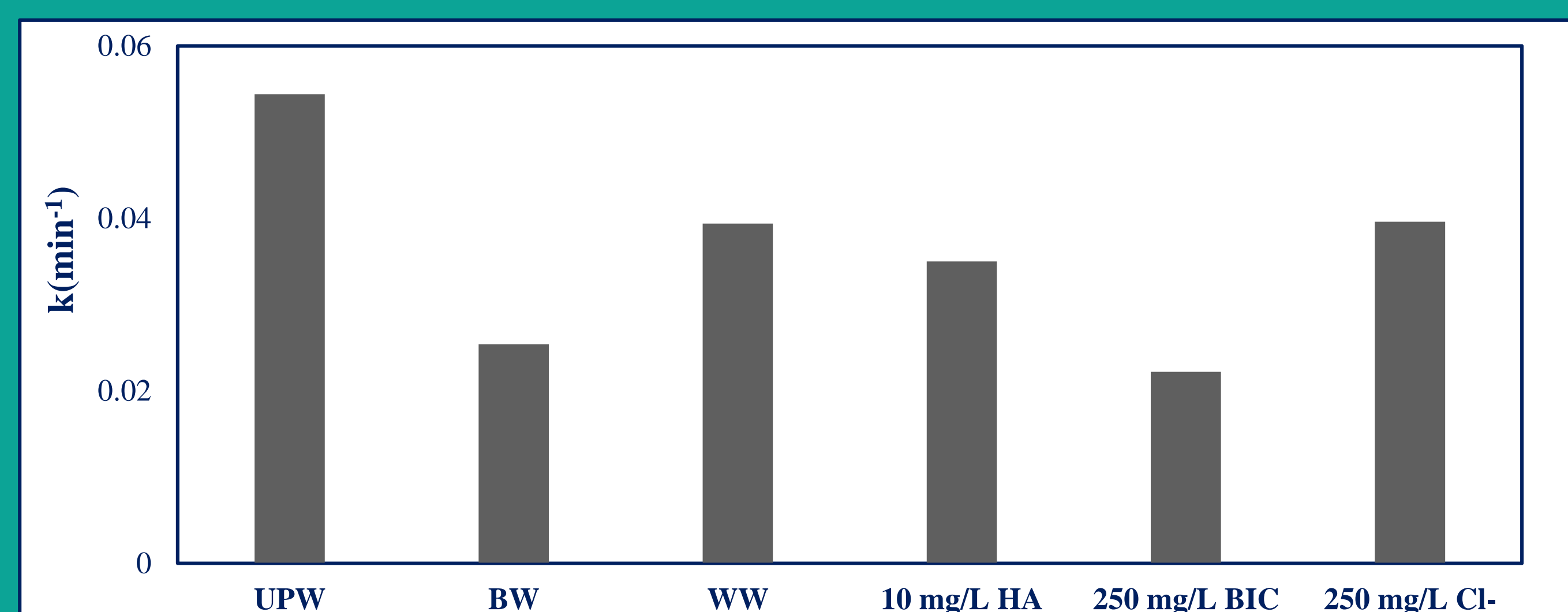


Figure 4. Rate constants of water matrices and water constituents.

Conclusions

In the present study, the EO degradation of VAL has been accomplished and the main conclusions observed from the investigation are:

- The type of supporting electrolyte appears to play a crucial role during the EO process.
- The performance of the treatment exhibited a strong pH-dependency, as the highest removal of the drug was achieved under low pH values.
- The highest efficiency of the process was observed at higher applied J and lower VAL concentration.
- The complexity of the environmental matrices hindered the efficiency of the process, which possibly associates to the presence of organic and inorganic ions in existence within actual waters matrices.

References

1. R.L. Webb et al., (2001). Exp. Clin. Cardiol. 6, 215-221.
2. S. Padmanabhan et al., (2012). Trends Genet. 28, 397-408.
3. O.S. Arvaniti et al., (2015). Total Environ. 524-525, 81-92.
4. K. Ikehata et al., (2006). Ozone-Sci. Eng. 28, 353-414.
5. P.V. Nidheesh et al., (2019). Chem. Electro. Chem. 6, 2124-2142.
6. C.A. Martinez-Huitle et al. (2006). Chem. Soc. Rev. 35, 1324-1340.

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