Electrochemical Mineralization Kinetics of Metformin

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Present work analyzes the kinetic study of mineralization during electro-oxidation on Ti/DSA (Ta_2O_5-Ir_2O_5) and combined electro-oxidation and electro-coagulation on stainless steel anode of an antidiabetic drug metformin hydrochloride (MET-HCl) in synthetic wastewater over a specific charge. Four different reaction orders (0.5, 1, 1.5 and 2) were tested using the integral analysis method by plotting TOC concentration terms over specific charges to determine the exact rate kinetics for the mineralization. The effect of applied current density was evaluated at 50 ppm of sodium sulphate as supporting electrolyte, and the effect of supporting electrolyte concentration was also assessed at a current density of 0.93 mA/cm² in 50 ppm MET-HCl solution. As a result of (i) electro-oxidation experiments on MET-HCl, carried out on Ti/DSA anode, and (ii) combined electro-oxidation and electro-coagulation experiments carried out on stainless steel anode, based on the R-squared value of the mineralization curves, the first-order reaction rate was proposed.

Keywords: Rate kinetics, Electro-oxidation, Electro-coagulation, Applied current density, Mineralization.

INTRODUCTION

Metformin (MET) is used as the first-line drug for treating type 2 diabetes worldwide [1] and is reported as one of the most used medical prescription drugs worldwide [2]. Metformin has been detected in a range of 0.06-3.10 g L⁻¹ and 1.2-118 g L⁻¹ in surface water and wastewater treatment plants (WWTPs) [3-6]. Metformin has been recognized as an endocrine disrupter to fish and is contagious at an environmentally relevant concentration (40 μg L⁻¹) [7]. Various processes, like solid-phase extraction, ozonation, photocatalytic degradation, are used to remove MET, but they are less efficient with poor recoveries and high energy consumption. Therefore, an efficient and ecofriendly method is to be implemented to remove MET from wastewater [8-12].

To the best of our knowledge and based on the literature, no previous work reported on the kinetic study on MET-HCl mineralization over specific charge during electro-oxidation experiments carried out on Ti/DSA anode and combined electro-oxidation and electro-coagulation experiments carried out on stainless steel anode. Ti/DSA electrodes have reported high efficiency and stability in the electrochemical oxidation of

refractory molecules [13]. Stainless steel had found effective in the mineralization of diclofenac sodium even without adding outside oxidant through the combined process of electro-oxidation and electro-coagulation [14]. Its electrical energy consumption can also be reduced by the utilization of process integration [15].

This study reports the kinetic study of mineralization of MET-HCl using the process of electro-oxidation on Ti/DSA (Ta_2O_5-Ir_2O_5) and combined electro-oxidation and electro-coagulation on stainless steel anode. The effect of different process parameters is studied. The mineralization curves of MET-HCl plotted for two processes are tested for different rate kinetics.

EXPERIMENTAL

Metformin hydrochloride (MET-HCl, $C_4H_{11}N_5$·HCl) of the pharmaceutical grade was used as the target organic pollutant in the study. It was kindly donated by M/s IOLCP, Barnala, India. Ti/DSA (Ta_2O_5-Ir_2O_5) plates (50 mm × 45 mm × 1 mm thick with Hook 60 mm × 8 mm × 1 mm thick) were purchased from Ti Anode Fabricator Pvt. Ltd., Chennai, India. Stainless steel 304 (50 mm × 45 mm × 1 mm thick with Hook 60 mm ×

8 mm × 1 mm thick) were purchased from local metal shop, Sangrur, India. Sodium carbonate anhydrous (Na_2CO_3) and sodium hydrogen carbonate ($NaHCO_3$) of AR grades were purchased from CDH, Mumbai, India. Orthophosphoric acid (H_3PO_4) and potassium hydrogen phthalate ($C_8H_5KO_4$) of HPLC grade were purchased from Loba Chemie Pvt. Ltd., Mumbai, India. Sodium sulphate (anhydrous) of SQ grade was procured from Thermo Fisher Scientific India Pvt. Ltd, Mumbai, India. All the solutions were prepared with ultrapure deionized water obtained with a Millipore water purification system (Merck progard®TS2). Total organic carbon was determined using a TOC-L Shimadzu TOC analyzer based on combustion catalytic oxidation.

Electrochemical experiments: All the electrochemical experiments of the MET-HCl were performed in a glass reactor of 250 mL in conjunction with a computer-controlled potentio-stat/galvanostat model SP-150 with EC Lab V10.33 software. Ti/DSA as the anode and SS-304 as cathode was used for the electro-oxidation experiments, whilst SS-304 electrode was used as anode plus cathode for the combined electro-oxidation and electro-coagulation experiments. Both electrodes were rectangle-shaped, with each having a working area of 90 cm^2 and a 5 mm inter-electrode gap was used.

All experiments were carried out using 200 mL synthetic wastewater carrying 50 ppm of MET-HCl at three different supporting electrolyte concentrations of 50, 75 and 100 ppm of Na_2SO_4 at three current densities of 0.67, 0.93 and 1.16 mA/cm^2. All the experiments were performed in duplicate and the average results were reported.

RESULTS AND DISCUSSION

Effect of applied current density on electro-oxidation of MET-HCl: To assess the effect of current density j_{app} (0.67, 0.93 and 1.16 mA/cm^2), we performed electro-oxidation experiments on 50 ppm MET-HCl solution supported with 50 ppm Na_2SO_4 as electrolyte.

Four different reaction orders (0.5, 1, 1.5 and 2) are tested by using the integral method of analysis by plotting TOC concentration terms over specific charges to find out the exact rate kinetics for the mineralization of MET-HCl on Ti/DSA anode. Fig. 1a shows the effect of the current density on the $2TOC_t^{0.5}-2TOC_0^{0.5}$ as a function of specific charge (Ah/L), for half order rate kinetics, (ii) Fig. 1b shows the effect of the current density on the linear variation of the natural logarithm of TOC_t/TOC_0 as a function of specific charge (Ah/L), for first-order kinetics, (iii) Fig. 1c shows the effect of the current density on
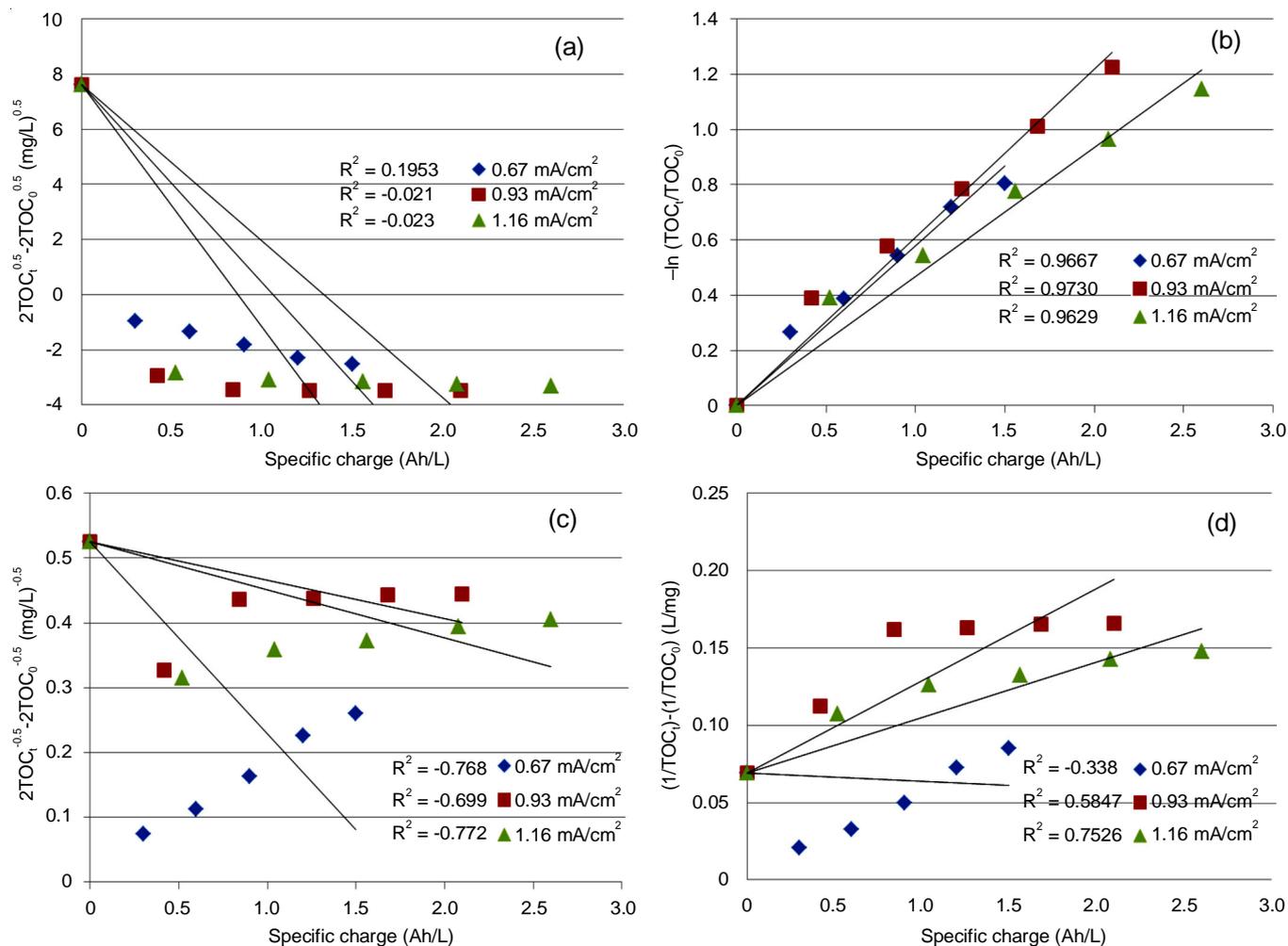

Fig. 1. Effect of the current density and specific charge (Ah/L) for the rate kinetics of electro-oxidation of MET-HCl on Ti/DSA anode (a) 0.5th order (b) 1st order (c) 1.5th order (d) 2nd order Conditions: 50 ppm MET-HCl, 50 ppm Na_2SO_4; SS = stainless steel

the $2TOC_t^{-0.5}-2TOC_0^{-0.5}$ as a function of specific charge, 1.5^{th} order kinetics, and (iv) Fig. 1d shows the effect of the current density on the $(1/TOC_t-1/TOC_0)$ as a function of specific charge (Ah/L), for 2nd order kinetics. For all plotted curves of different orders, associated correlation coefficients (R-squared value) are displayed in Table-1. Consequently, high values of correlation coefficients confirmed the pseudo-first-order kinetics for mineralization of MET-HCl and for kinetics analysis, the rate is calculated by a pseudo-first-order equation as follows [16]:

$$\ln\left(\frac{TOC_t}{TOC_o}\right) = -kQ \tag{1}$$

where, TOC_t = residual MET-HCl TOC concentration; TOC_0 = initial MET-HCl TOC concentration; K = pseudo first order rate constant (L/Ah); Q = specific charge (Ah/L).

Effect of Na_2SO_4 concentration on electro-oxidation of MET-HCl: To assess the effect of Na_2SO_4 concentration (50, 75 and 100 ppm), we performed electro-oxidation experiments on 50 ppm MET-HCl solution at a current density of 0.93 mA/cm². Four different reaction orders (0.5, 1, 1.5 and 2) are tested by using the integral method of analysis by plotting TOC concentration terms over specific charges to find out the exact rate kinetics for the mineralization of MET-HCl on Ti/DSA anode. Fig. 2a shows the effect of Na_2SO_4 concentration on the $2TOC_t^{0.5}-2TOC_0^{0.5}$ as a function of specific charge (Ah/L), for half order rate kinetics; Fig. 2b shows the effect of Na_2SO_4 concentration on the linear variation of the natural logarithm of TOC_t/TOC_0 as a function of specific charge (Ah/L), for first-order kinetics; Fig. 2c shows the effect of Na_2SO_4 concentration on the $2TOC_t^{-0.5}-2TOC_0^{-0.5}$ as a function of specific charge, 1.5^{th} order kinetics and Fig. 2d shows the effect of Na_2SO_4 concen-tration on the $(1/TOC_t-1/TOC_0)$ as a function of specific charge (Ah/L), for 2nd order kinetics. For all plotted curves of different orders, associated correlation coefficients (R-squared value) are displayed in Table-1. In this case, also, straight-line funct-ionality between the natural logarithm of TOC_t/TOC_0 and specific charge (Ah/L) with high values of

TABLE-1
RATE KINETICS OF ELECTRO-OXIDATION
OF MET-HCl AT Ti/DSA ANODE

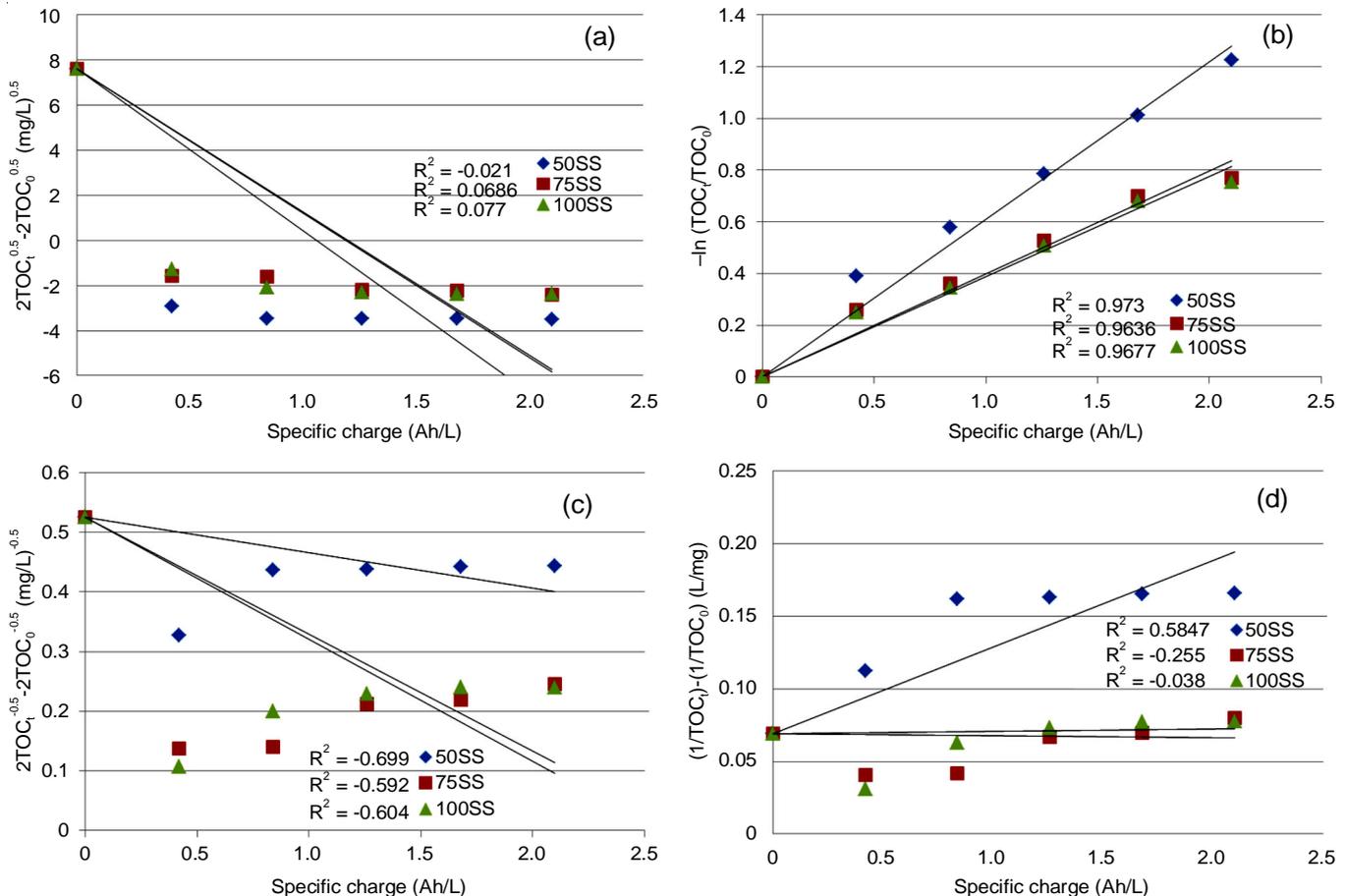| Current density (mA/cm²)	Na₂SO₄ conc. (ppm)	R-squared values of chart of different orders			
		05th	1st	1.5^{th}	2nd
Mineralization					
0.67	50	0.1953	0.9667	-0.768	-0.3380
0.93	50	-0.0210	0.9730	-0.699	0.5847
1.16	50	-0.0230	0.9629	-0.772	0.7526
0.93	75	0.0686	0.9636	-0.592	-0.2550
0.93	100	0.0770	0.9677	-0.604	-0.0380

Fig. 2. Effect of Na_2SO_4 concentration and specific charge (Ah/L) for the rate kinetics of electro-oxidation of MET-HCl on Ti/DSA anode (a) 0.5^{th} order (b) 1st order (c) 1.5^{th} order (d) 2nd order Conditions: 50 ppm MET-HCl, Current density 0.93 mA/cm²; SS = stainless steel

correlation coeffici-ents confirm the pseudo-first-order kinetics for mineralization of MET-HCl and kinetics analysis, the rate is calculated by a pseudo-first-order eqn. 1.

Effect of applied current density on combined electro-oxidation and electro-coagulation of MET-HCl: Four different reaction orders (0.5, 1, 1.5 and 2) are tested by using an integral method of analysis by plotting TOC concentration terms over specific charges to find out the exact rate kinetics for the mineralization of MET-HCl on stainless steel anode. Fig. 3a shows the effect of current density on the $2TOC_t^{0.5} - 2TOC_0^{0.5}$ as a function of specific charge (Ah/L), for half order rate kinetics; Fig. 3b shows the effect of the current density on the linear variation of the natural logarithm of TOC_t/TOC_0 as a function of specific charge (Ah/L), for first-order kinetics Fig. 3c shows the effect of the current density on the $2TOC_t^{-0.5} - 2TOC_0^{-0.5}$ as a function of specific charge, 1.5^{th} order kinetics and Fig. 3d shows the effect of the current density on the $(1/TOC_t - 1/TOC_0)$ as a function of specific charge (Ah/L), for 2nd order kinetics. For all plotted curves of different orders, associated correlation coefficients (R^2 value) are shown in Table-2. Consequently, high values of R-squared confirmed the adherence to pseudo-first-order kinetics for mineralization of MET-HCl for stainless steel anode and for kinetics analysis, the rate is calculated by a pseudo-first-order eqn. 1.

TABLE-2
RATE KINETICS OF COMBINED ELECTRO-OXIDATION AND ELECTRO-COAGULATION OF MET-HCl AT SS ANODE

Current density (mA/cm²)	Na₂SO₄ conc. (ppm)	R-squared values of chart of different orders			
		05th	1st	1.5th	2nd
		Mineralization			
0.67	50	0.0115	0.9646	0.2732	0.9341
0.93	50	0.0783	0.9662	0.8219	0.8362
1.16	50	0.1231	0.9619	0.7256	0.9796
0.93	75	0.0369	0.9745	0.8713	0.9374
0.93	100	0.0992	0.96	-0.422	0.9934

Effect of Na₂SO₄ concentration on combined electro-oxidation and electro-coagulation of MET-HCl: Four different reaction orders (0.5, 1, 1.5 and 2) are tested by using an integral method of analysis by plotting TOC concentration terms over specific charges to find out the exact rate kinetics for the mineralization of MET-HCl on stainless steel anode. Fig. 4a shows the effect of the Na₂SO₄ concentration on the $2TOC_t^{0.5} - 2TOC_0^{0.5}$ as a function of specific charge (Ah/L), for half order rate kinetics, Fig. 4b shows the effect of Na₂SO₄ concen-tration on the linear variation of the natural logarithm of TOC_t/TOC_0 as a function of specific charge (Ah/L) for first-order kinetics, Fig. 4c shows the effect of Na₂SO₄ concentration
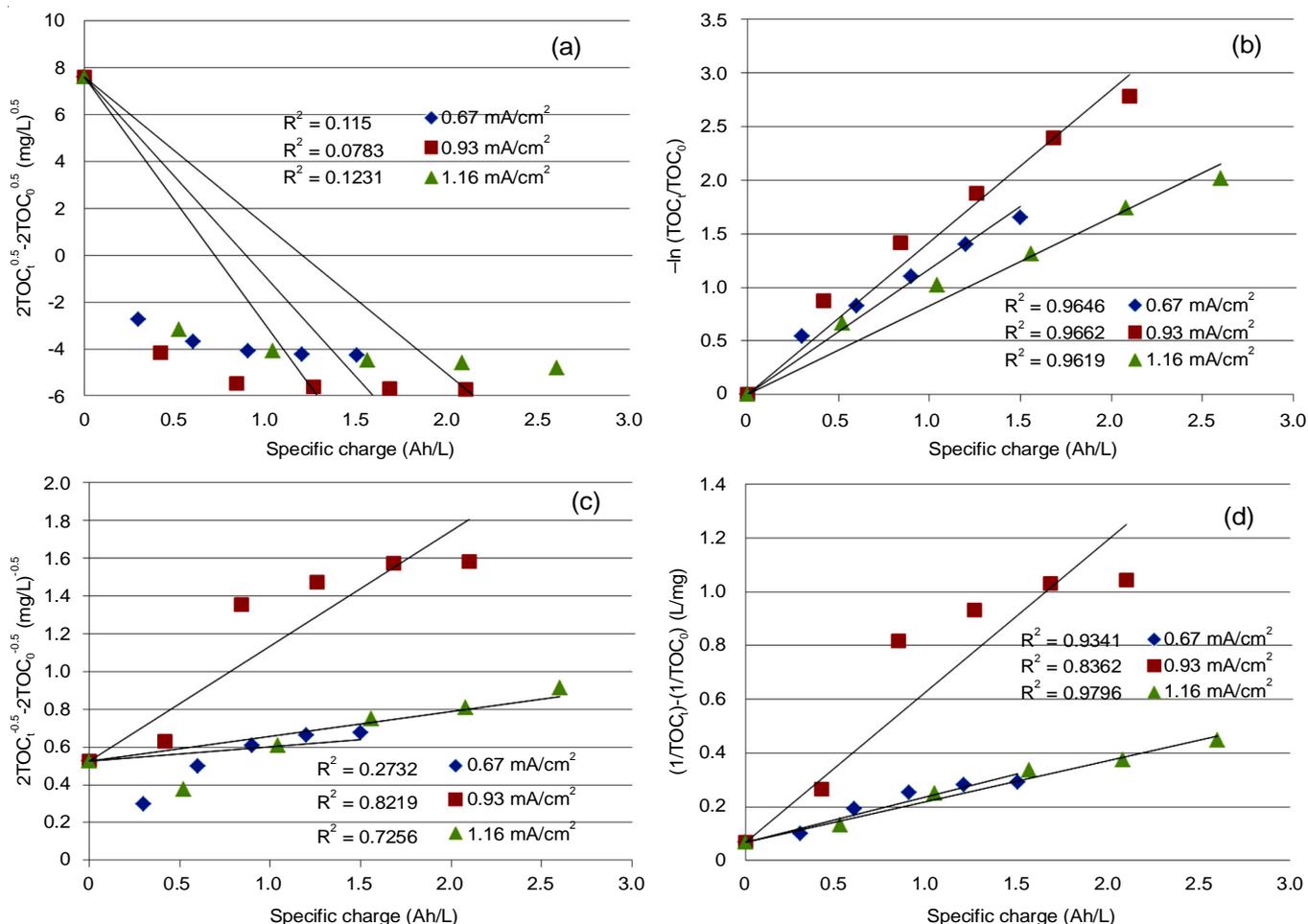

Fig. 3. Effect of current density and specific charge (Ah/L) for the rate kinetics of combined electro-oxidation and electro-coagulation of MET-HCl on stainless steel anode (a) 0.5^{th} order (b) 1st order (c) 1.5^{th} order (d) 2nd order Conditions: 50 ppm MET-HCl, 50 ppm Na₂SO₄; SS = stainless steel
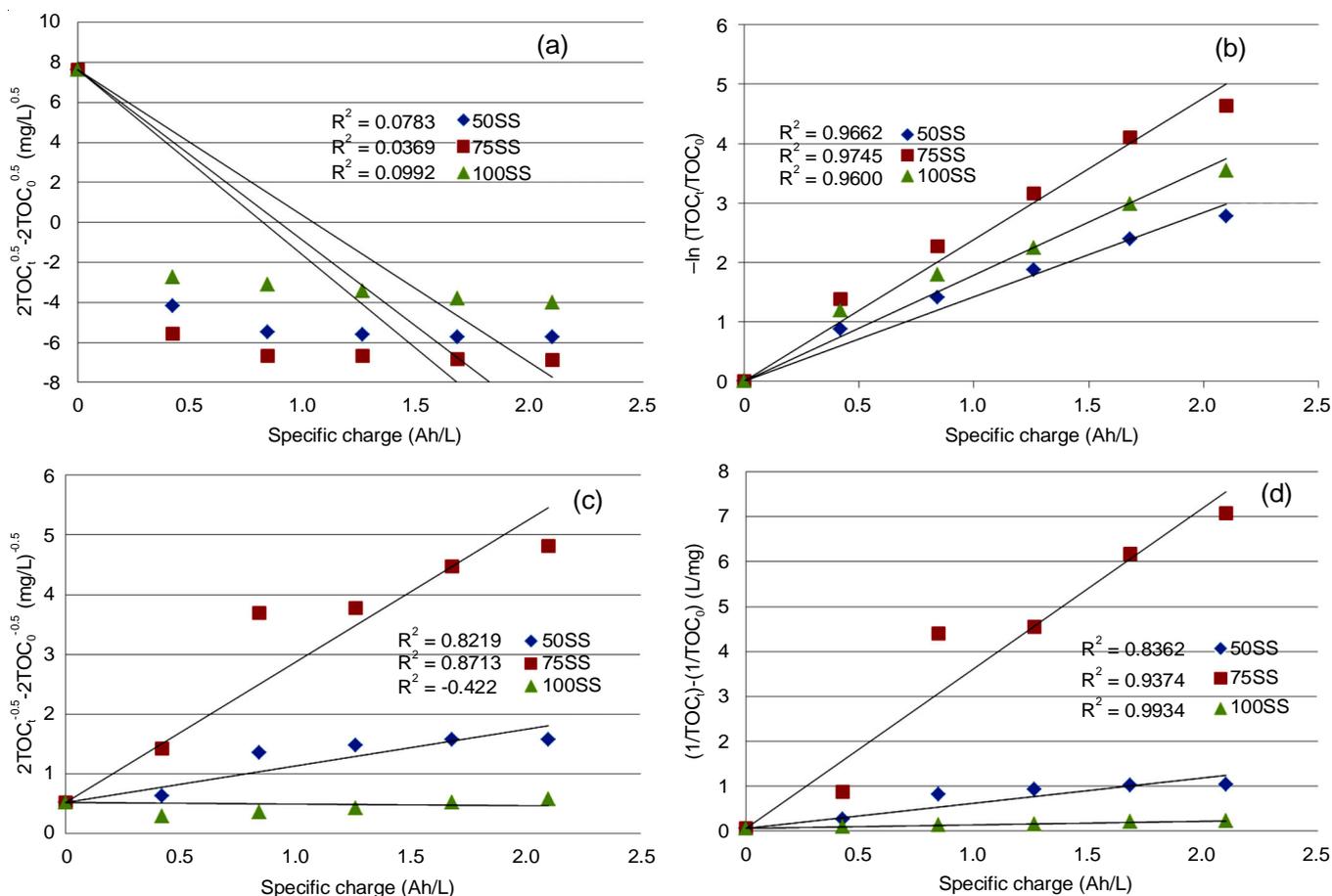
Fig. 4. Effect of the Na_2SO_4 concentration and specific charge (Ah/L) for the rate kinetics of combined electro-oxidation and electro-coagulation of MET-HCl on SS anode (a) 0.5^{th} order (b) 1st order (c) 1.5^{th} order (d) 2nd order (Conditions: 50 ppm MET-HCl, Current density 0.93 mA/cm^2), SS = stainless steel

on the $2TOC_t^{-0.5} - 2TOC_0^{-0.5}$ as a function of specific charge, for 1.5^{th} order kinetics and Fig. 4d shows the effect of Na_2SO_4 concentration on the $(1/TOC_t - 1/TOC_0)$ as a function of specific charge (Ah/L) for 2nd order kinetics. For all plotted curves of different orders, associated correlation coefficients (R^2 value) are shown in Table-2. Consequently, high values of R-squared confirm the adherence to pseudo-first-order kinetics for mineralization of MET-HCl for stainless steel anode as well and for kinetics analysis, the rate is calculated by a pseudo-first-order eqn. 1.

Conclusion

In present investigation, the kinetic study of mineralization of antidiabetic drug MET-HCl in synthetic wastewater was studied by electro-oxidation and combined electro-oxidation and electro-coagulation on Ti/DSA (Ta_2O_5-Ir_2O_5) and stainless steel anode, respectively, in a batch operation. The effect of applied current density was evaluated at 50 ppm of sodium sulphate (Na_2SO_4) as supporting electrolyte and the effect of supporting electrolyte concentration was also evaluated at a current density of 0.93 mA/cm^2 in 50 ppm MET-HCl solution. Four different reaction orders (0.5, 1, 1.5 and 2) are tested by using the integral method of analysis by plotting TOC concentration term over specific charge to find out the exact rate kinetics for the mineralization of MET-HCl on

stainless steel anode. The electrochemical mineralization of MET-HCl depended on the anode type. For mineralization of MET-HCl for both Ti/DSA (Ta_2O_5-Ir_2O_5) and stainless steel anode, high values of R-squared were obtained for mineralization curves of MET-HCl for both Ti/DSA (Ta_2O_5-Ir_2O_5) and stainless steel anode, which confirmed for pseudo-first-order kinetics for mineralization of MET-HCl on both the anodes.

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