

**Mechanisms for degradation and transformation of  $\beta$ -blocker atenolol via electrocoagulation, electro-Fenton, and electro-Fenton-*like* processes**

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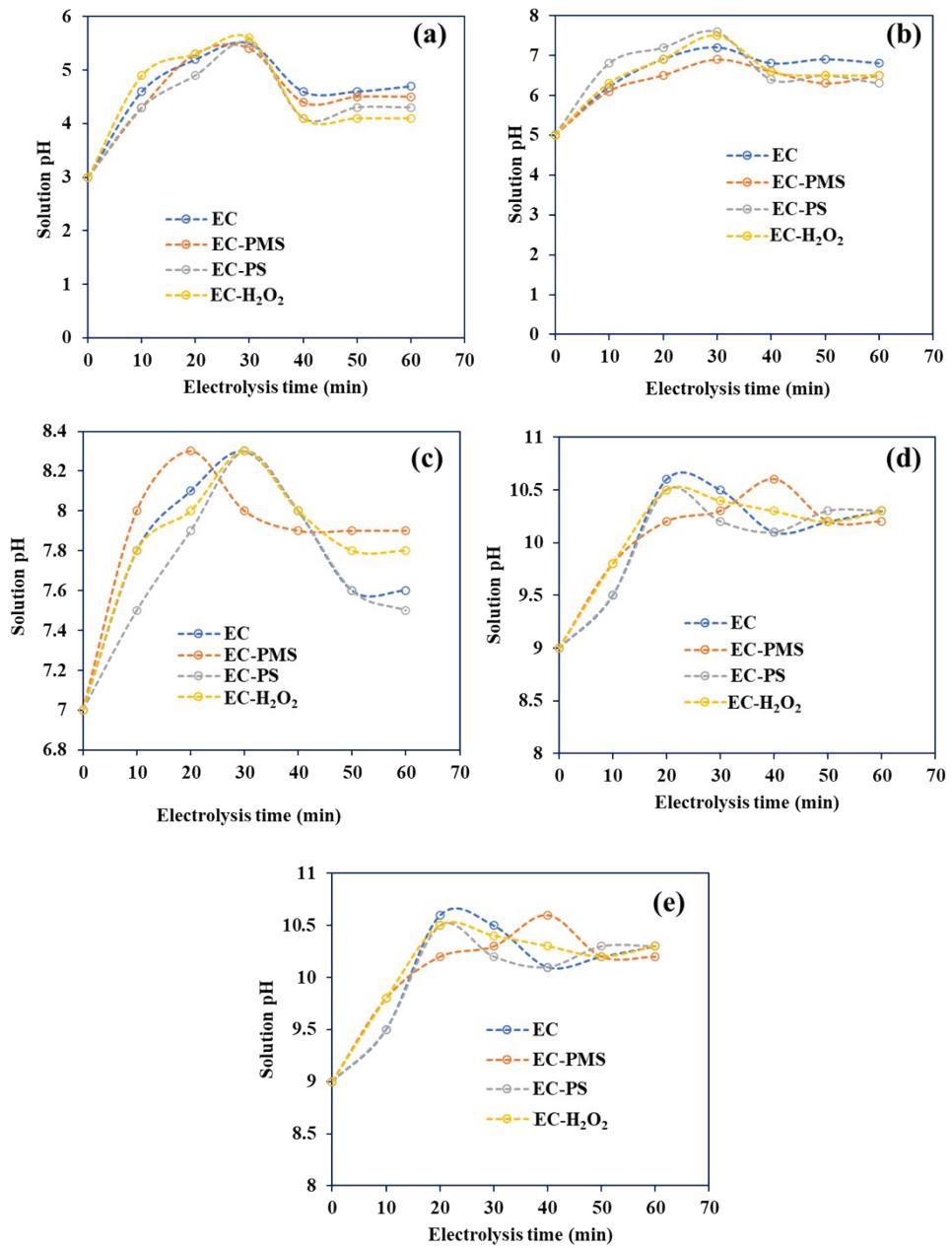
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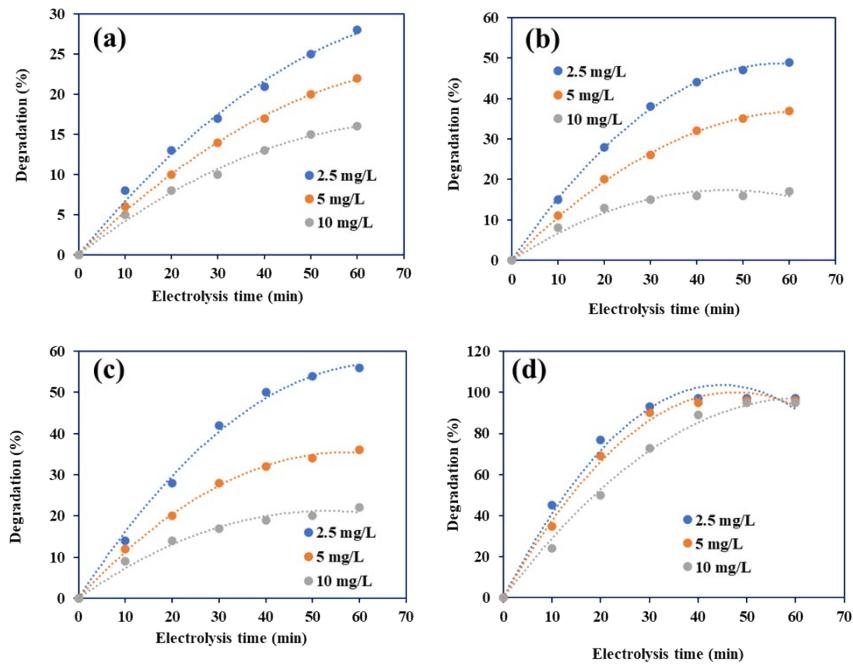
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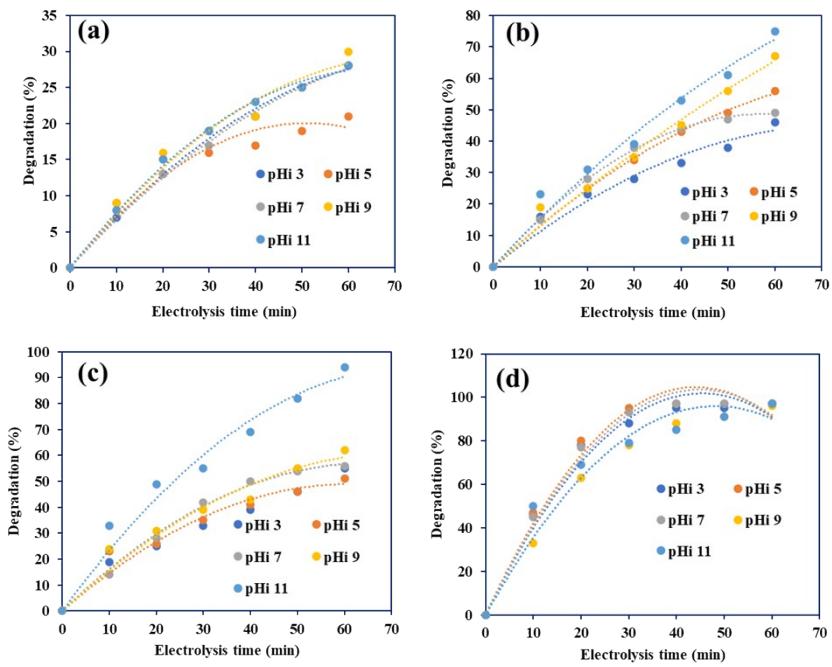
<sup>1</sup>These authors contributed equally to this work.



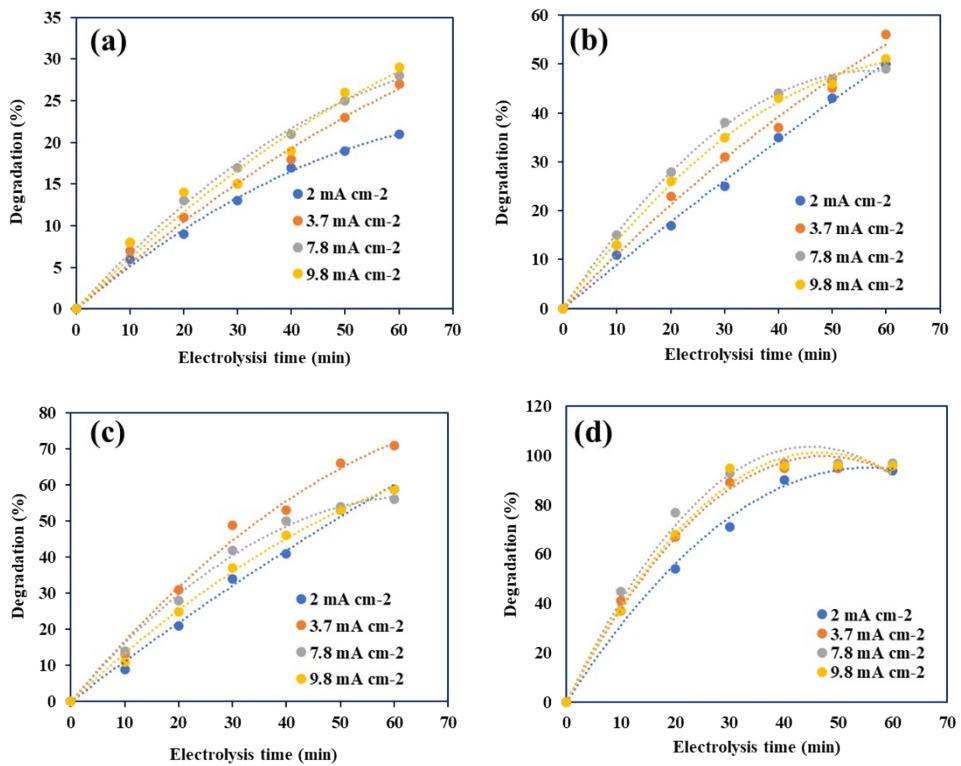
**Fig. S1** Variation of solution pH as a function of electrolysis at different electrochemical process started with different initial solution pH (a) 3, (b) 5, (c) 7, (d) 9 and (e) 11. Conditions:  $C_{\text{NaCl}} = 1000 \text{ mg L}^{-1}$ ,  $C_{\text{Oxidant}} = 0.10 \text{ mM}$ ,  $C_{\text{AT}} = 2.5 \text{ mg L}^{-1}$ , and  $7.8 \text{ mA cm}^{-2}$ .



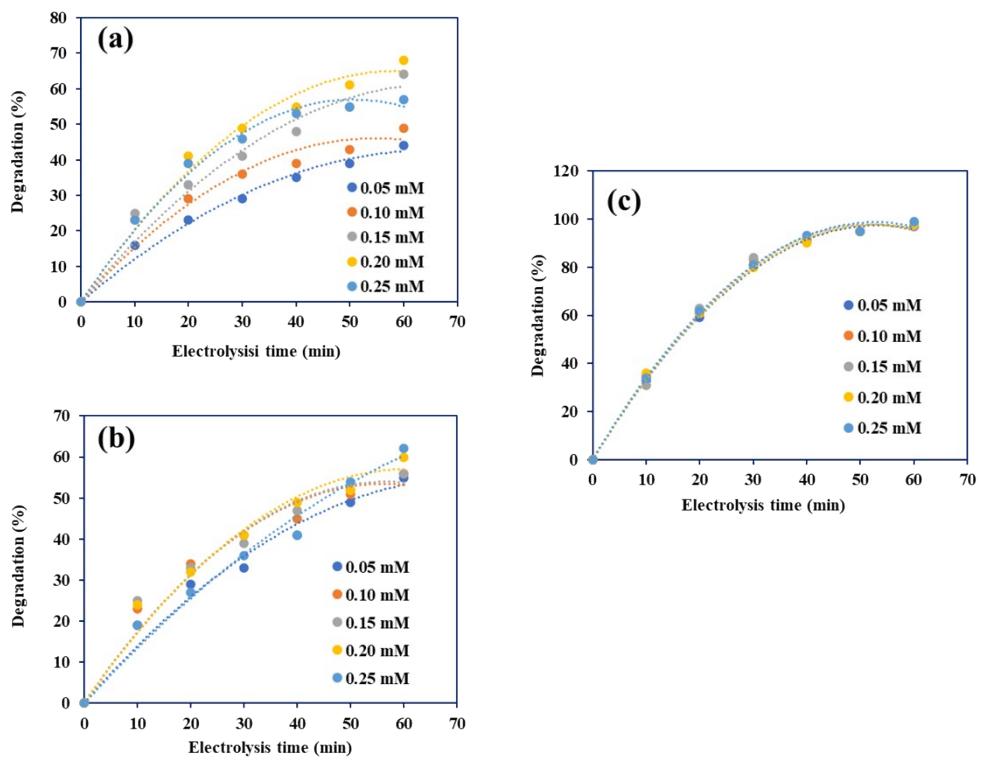
**Fig. S2** Influence of initial atenolol concentration on degradation profile by different electrochemical process; (a) EC, (b) EC-PMS, (c) EC-PS and (d) EC-H<sub>2</sub>O<sub>2</sub>. Conditions: C<sub>NaCl</sub> = 1000 mg L<sup>-1</sup>, pH<sub>i</sub> = 7, and 7.8 mA cm<sup>-2</sup>.



**Fig. S3** Variation of atenolol degradation profile as a function of electrolysis time at different initial solution pH (a) EC; (b) EC-PMS; (c) EC-PS and (d) EC-H<sub>2</sub>O<sub>2</sub>.



**Fig. S4** Variation of atenolol degradation profile as a function of electrolysis time at different current densities (a) EC; (b) EC-PMS; (c) EC-PS and (d) EC-H<sub>2</sub>O<sub>2</sub>.



**Fig. S5** Variation of atenolol degradation profile as a function of electrolysis time at oxidant concentration (a) EC-PMS; (b) EC-PS and (c) EC-H<sub>2</sub>O<sub>2</sub>.

**Table S1** Potential reactive free radicals and oxidative species formed in the various electrochemical processes<sup>1–3</sup>

|                                      | <b>NaCl</b>  | <b>Na<sub>2</sub>CO<sub>3</sub></b>   | <b>NaHCO<sub>3</sub></b>   | <b>Na<sub>2</sub>SO<sub>4</sub></b>                           | <b>NaNO<sub>3</sub></b>                                       |
|--------------------------------------|--|---|--|---|---|
| <b>EC</b>                            | ·OH, O <sub>2</sub> <sup>·-</sup> , Cl <sub>2</sub> / HOCl                             | ·OH, O <sub>2</sub> <sup>·-</sup> , CO <sub>3</sub> <sup>2-</sup>                             | ·OH, O <sub>2</sub> <sup>·-</sup> , HCO <sub>3</sub> <sup>2-</sup>                             | ·OH, O <sub>2</sub> <sup>·-</sup>                             | ·OH, O <sub>2</sub> <sup>·-</sup>                             |
| <b>EC-PMS</b>                        | SO <sub>4</sub> <sup>2-</sup> , SO <sub>5</sub> <sup>2-</sup> , Cl <sub>2</sub> / HOCl | SO <sub>4</sub> <sup>2-</sup> , CO <sub>3</sub> <sup>2-</sup>                                 | SO <sub>4</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>2-</sup>                                 | SO <sub>4</sub> <sup>2-</sup> , SO <sub>5</sub> <sup>2-</sup> | SO <sub>4</sub> <sup>2-</sup> , SO <sub>5</sub> <sup>2-</sup> |
| <b>EC-PS</b>                         | SO <sub>4</sub> <sup>2-</sup> , SO <sub>5</sub> <sup>2-</sup> , Cl <sub>2</sub> / HOCl | SO <sub>4</sub> <sup>2-</sup> , SO <sub>5</sub> <sup>2-</sup> , CO <sub>3</sub> <sup>2-</sup> | SO <sub>4</sub> <sup>2-</sup> , SO <sub>5</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>2-</sup> | SO <sub>4</sub> <sup>2-</sup> , SO <sub>5</sub> <sup>2-</sup> | SO <sub>4</sub> <sup>2-</sup> , SO <sub>5</sub> <sup>2-</sup> |
| <b>EC-H<sub>2</sub>O<sub>2</sub></b> | ·OH, O <sub>2</sub> <sup>·-</sup> , Cl <sub>2</sub> / HOCl                             | ·OH, O <sub>2</sub> <sup>·-</sup> , CO <sub>3</sub> <sup>2-</sup>                             | ·OH, O <sub>2</sub> <sup>·-</sup> , HCO <sub>3</sub> <sup>2-</sup>                             | ·OH, O <sub>2</sub> <sup>·-</sup>                             | ·OH, O <sub>2</sub> <sup>·-</sup>                             |

- 1 X. Liu, L. Fang, Y. Zhou, T. Zhang and Y. Shao, *J. Environ. Sci. (China)*, 2013, **25**, 1519–1528.
- 2 E. Isarain-Chávez, C. Arias, P. L. Cabot, F. Centellas, R. M. Rodríguez, J. A. Garrido and E. Brillas, *Appl. Catal. B Environ.*, 2010, **96**, 361–369.
- 3 X. Liu, T. Zhang, Y. Zhou, L. Fang and Y. Shao, *Chemosphere*, 2013, **93**, 2717–2724.

**Table S2.** Transformation products of atenolol in different electrochemical coagulation (EC) conditions (✓ - detected and × - not detected)

| Atenolol and its transformation products | mass to charge ( <i>m/z</i> ) | EC   |                                 |                    |                                 |                   |
|--|-------------------------------|------|---------------------------------|--------------------|---------------------------------|-------------------|
|  |                               | NaCl | Na <sub>2</sub> CO <sub>3</sub> | NaHCO <sub>3</sub> | Na <sub>2</sub> SO <sub>4</sub> | NaNO <sub>3</sub> |
| DP299                                    | 299                           | ✓    | ✓                               | ✓                  | ✓                               | ✓                 |
| DP283                                    | 283                           | ✓    | ✓                               | ✓                  | ✓                               | ✓                 |
| DP267                                    | 267                           | ✓    | ✓                               | ✓                  | ✓                               | ✓                 |
| DP255                                    | 255                           | ✓    | ✓                               | ✓                  | ✓                               | ✓                 |
| DP238                                    | 238                           | ✓    | ✓                               | ✓                  | ✓                               | ✓                 |
| DP224                                    | 224                           | ✓    | ✓                               | ✓                  | ✓                               | ✓                 |
| DP207                                    | 207                           | ✓    | ✓                               | ✓                  | ✓                               | ✓                 |
| DP194                                    | 194                           | ✓    | ✓                               | ✓                  | ✓                               | ✗                 |
| DP189                                    | 189                           | ✓    | ✓                               | ✓                  | ✓                               | ✓                 |
| DP151                                    | 151                           | ✓    | ✓                               | ✓                  | ✓                               | ✓                 |
| DP134                                    | 134                           | ✓    | ✓                               | ✓                  | ✓                               | ✓                 |

**Table S3.** Transformation products of atenolol by EF-*like* (EC-PMS) processes in the presence of various co-ions (✓ - detected and × - not detected)

| Atenolol and its transformation products | mass to charge ( <i>m/z</i> ) | EC-PMS |                                 |                    |                                 |                   |
|--|-------------------------------|--------|---------------------------------|--------------------|---------------------------------|-------------------|
|  |                               | NaCl   | Na <sub>2</sub> CO <sub>3</sub> | NaHCO <sub>3</sub> | Na <sub>2</sub> SO <sub>4</sub> | NaNO <sub>3</sub> |
| DP299                                    | 299                           | ✓      | ✓                               | ×                  | ✓                               | ✓                 |
| DP283                                    | 283                           | ✓      | ✓                               | ×                  | ✓                               | ✓                 |
| DP267                                    | 267                           | ✓      | ✓                               | ✓                  | ✓                               | ✓                 |
| DP255                                    | 255                           | ✓      | ✗                               | ✓                  | ✓                               | ✓                 |
| DP238                                    | 238                           | ✓      | ✓                               | ✓                  | ✓                               | ✓                 |
| DP224                                    | 224                           | ✓      | ✓                               | ✓                  | ✓                               | ✓                 |
| DP207                                    | 207                           | ✓      | ✓                               | ✓                  | ✗                               | ✓                 |
| DP194                                    | 194                           | ✓      | ✓                               | ✓                  | ✓                               | ✓                 |
| DP189                                    | 189                           | ✓      | ✗                               | ✗                  | ✓                               | ✗                 |
| DP151                                    | 151                           | ✓      | ✓                               | ✓                  | ✓                               | ✓                 |
| DP134                                    | 134                           | ✓      | ✓                               | ✗                  | ✓                               | ✓                 |

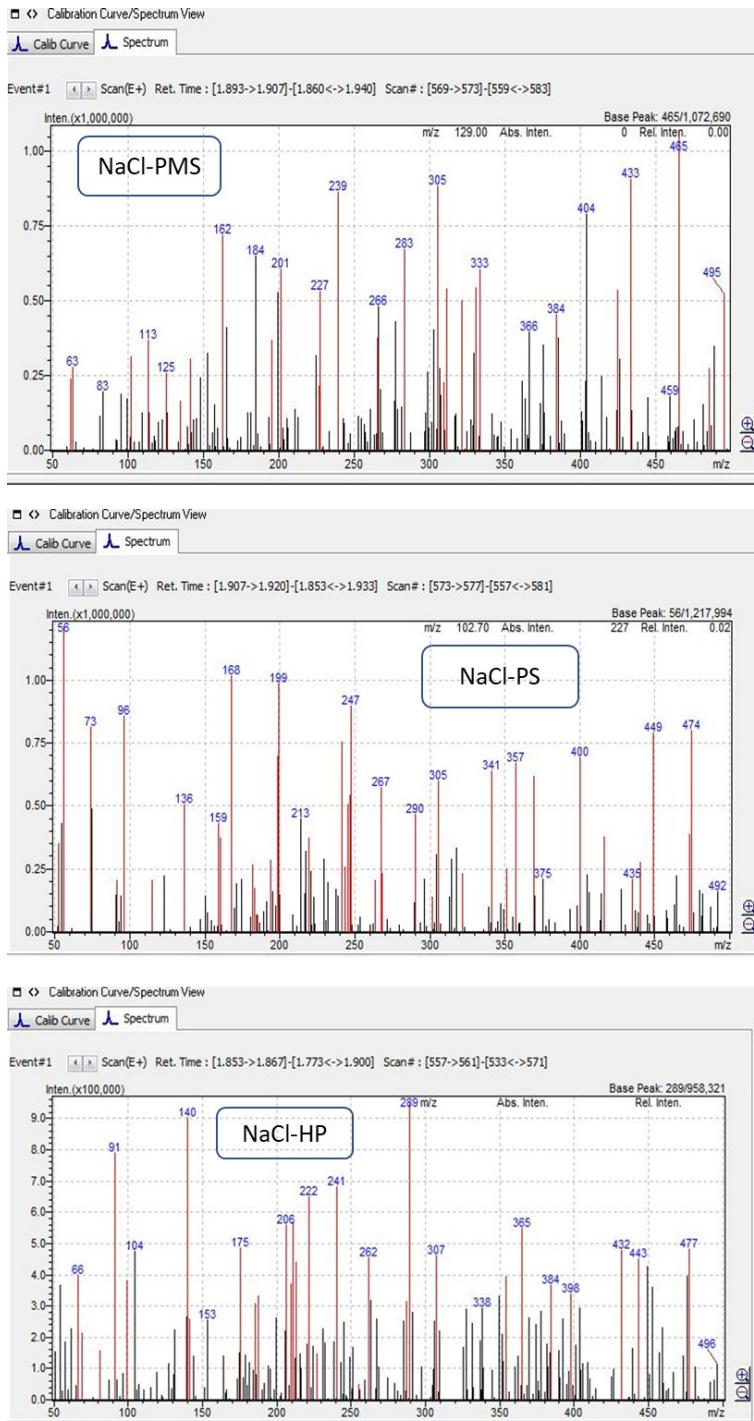
**Table S4.** Transformation products of atenolol by EF-*like* (EC-PS) processes in the presence of various co-ions (✓ - detected and × - not detected)

| Atenolol and its transformation products | mass to charge ( <i>m/z</i> ) | EC-PS |                                 |                    |                                 |                   |
|--|-------------------------------|-------|---------------------------------|--------------------|---------------------------------|-------------------|
|  |                               | NaCl  | Na <sub>2</sub> CO <sub>3</sub> | NaHCO <sub>3</sub> | Na <sub>2</sub> SO <sub>4</sub> | NaNO <sub>3</sub> |
| DP299                                    | 299                           | ×     | ✓                               | ✓                  | ✓                               | ✓                 |
| DP283                                    | 283                           | ×     | ×                               | ✓                  | ✓                               | ✓                 |
| DP267                                    | 267                           | ✓     | ✓                               | ✓                  | ✓                               | ✓                 |
| DP255                                    | 255                           | ×     | ×                               | ✓                  | ✓                               | ✓                 |
| DP238                                    | 238                           | ✓     | ✓                               | ×                  | ✓                               | ✓                 |
| DP224                                    | 224                           | ✓     | ✓                               | ✓                  | ✓                               | ✓                 |
| DP207                                    | 207                           | ×     | ✓                               | ✓                  | ✓                               | ✓                 |
| DP194                                    | 194                           | ✓     | ✓                               | ✓                  | ✓                               | ✓                 |
| DP189                                    | 189                           | ✓     | ✓                               | ✓                  | ✓                               | ×                 |
| DP151                                    | 151                           | ✓     | ✓                               | ×                  | ×                               | ✓                 |
| DP134                                    | 134                           | ×     | ×                               | ✓                  | ×                               | ×                 |

**Table S5.** Transformation products of atenolol by EF (EC-H<sub>2</sub>O<sub>2</sub>) processes in the presence of various co-ions (✓ - detected and ✗ - not detected)

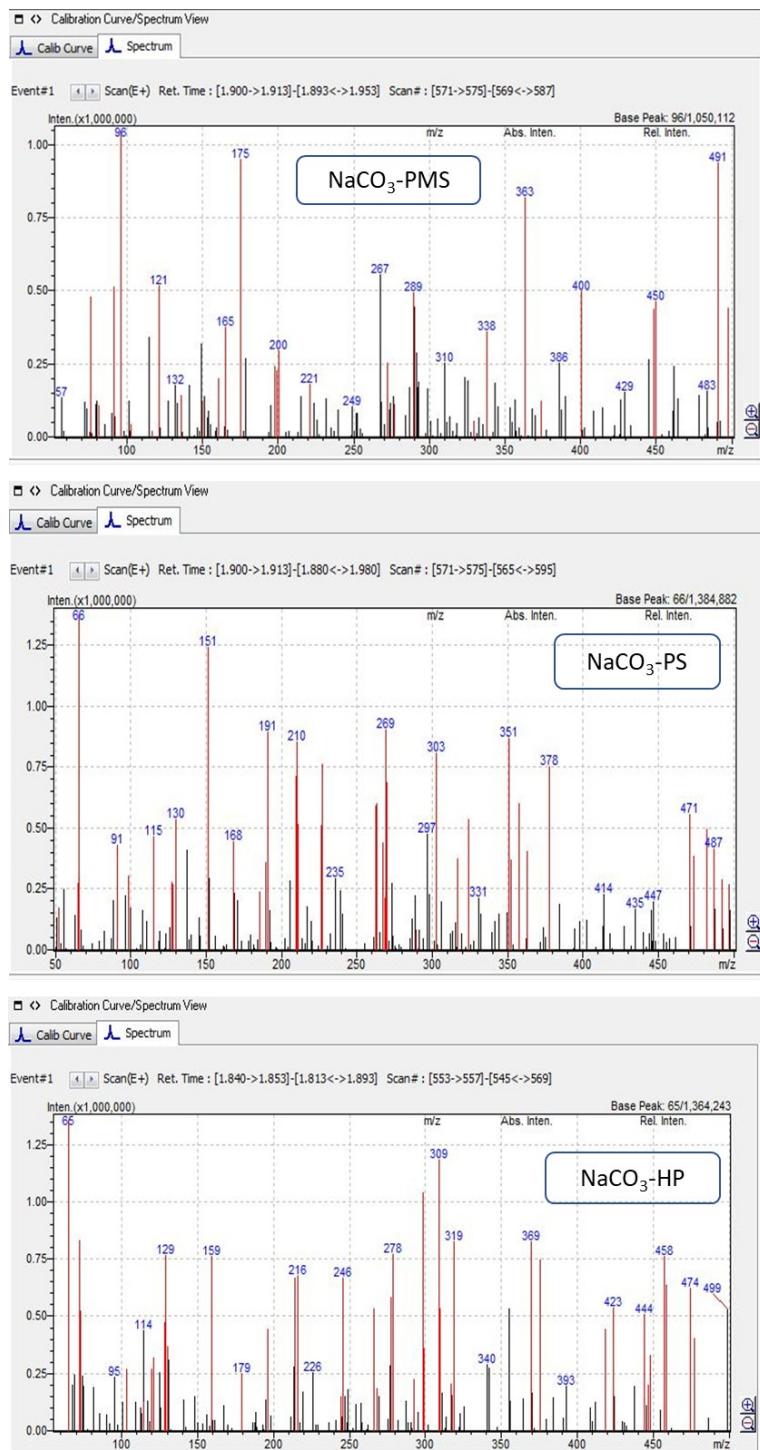
| Atenolol and its transformation products | mass to charge ( <i>m/z</i> ) | EC-HP |                                 |                    |                                 |                   |
|--|-------------------------------|-------|---------------------------------|--------------------|---------------------------------|-------------------|
|  |                               | NaCl  | Na <sub>2</sub> CO <sub>3</sub> | NaHCO <sub>3</sub> | Na <sub>2</sub> SO <sub>4</sub> | NaNO <sub>3</sub> |
| DP299                                    | 299                           | ✓     | ✓                               | ✓                  | ✗                               | ✗                 |
| DP283                                    | 283                           | ✗     | ✗                               | ✓                  | ✓                               | ✓                 |
| DP267                                    | 267                           | ✓     | ✓                               | ✓                  | ✓                               | ✓                 |
| DP255                                    | 255                           | ✓     | ✓                               | ✗                  | ✓                               | ✓                 |
| DP238                                    | 238                           | ✓     | ✗                               | ✓                  | ✓                               | ✓                 |
| DP224                                    | 224                           | ✓     | ✓                               | ✓                  | ✓                               | ✓                 |
| DP207                                    | 207                           | ✓     | ✗                               | ✗                  | ✓                               | ✓                 |
| DP194                                    | 194                           | ✓     | ✗                               | ✓                  | ✓                               | ✓                 |
| DP189                                    | 189                           | ✓     | ✓                               | ✗                  | ✗                               | ✓                 |
| DP151                                    | 151                           | ✓     | ✗                               | ✓                  | ✓                               | ✓                 |
| DP134                                    | 134                           | ✗     | ✗                               | ✗                  | ✓                               | ✓                 |

## LS-MS spectra of atenolol degradation



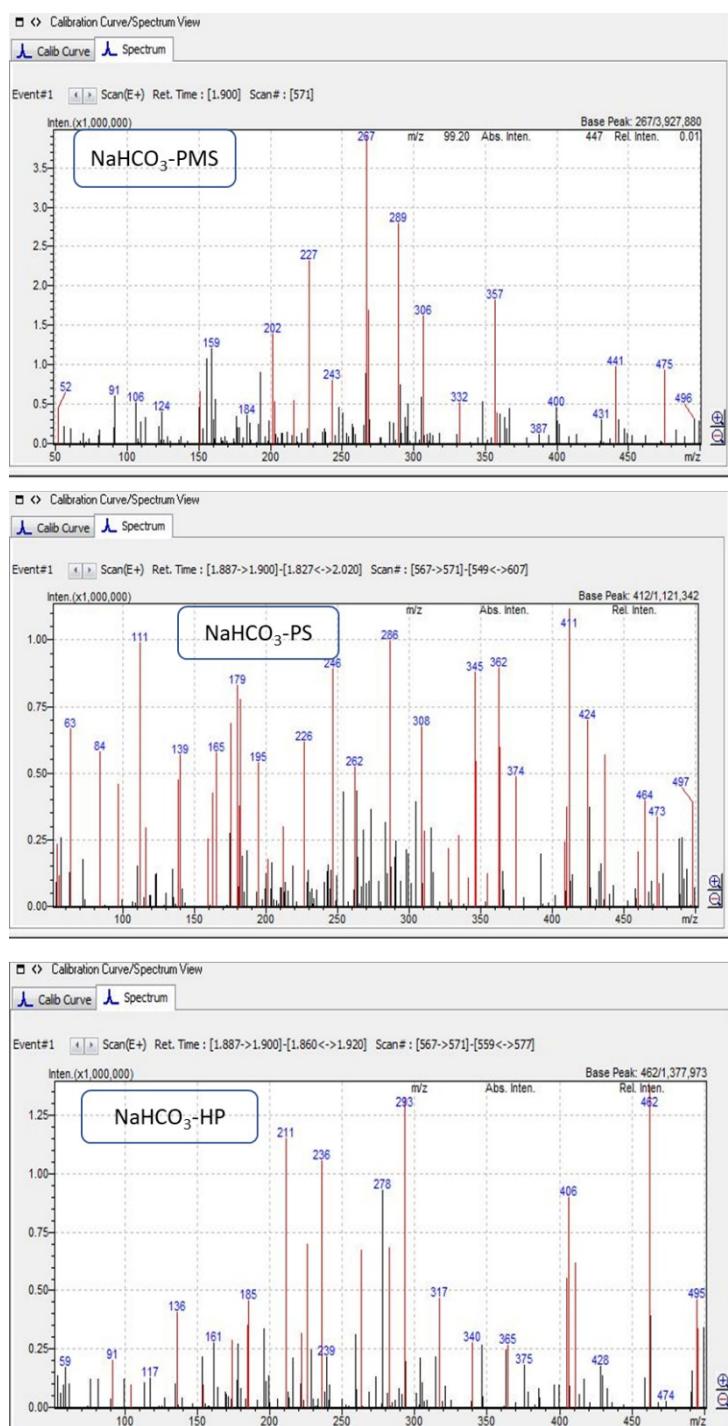
**Fig. S6** LC-MS spectra of samples obtained using EC in the presence of PMS, PS, and H<sub>2</sub>O<sub>2</sub>. Conditions: C<sub>ATL</sub> = 2.5 mg L<sup>-1</sup>, C<sub>NaCl</sub> = 1000 mg L<sup>-1</sup>, C<sub>Oxidant</sub> = 0.15 mM, initial solution pH<sub>i</sub> =

7, and 60 min electrolysis.



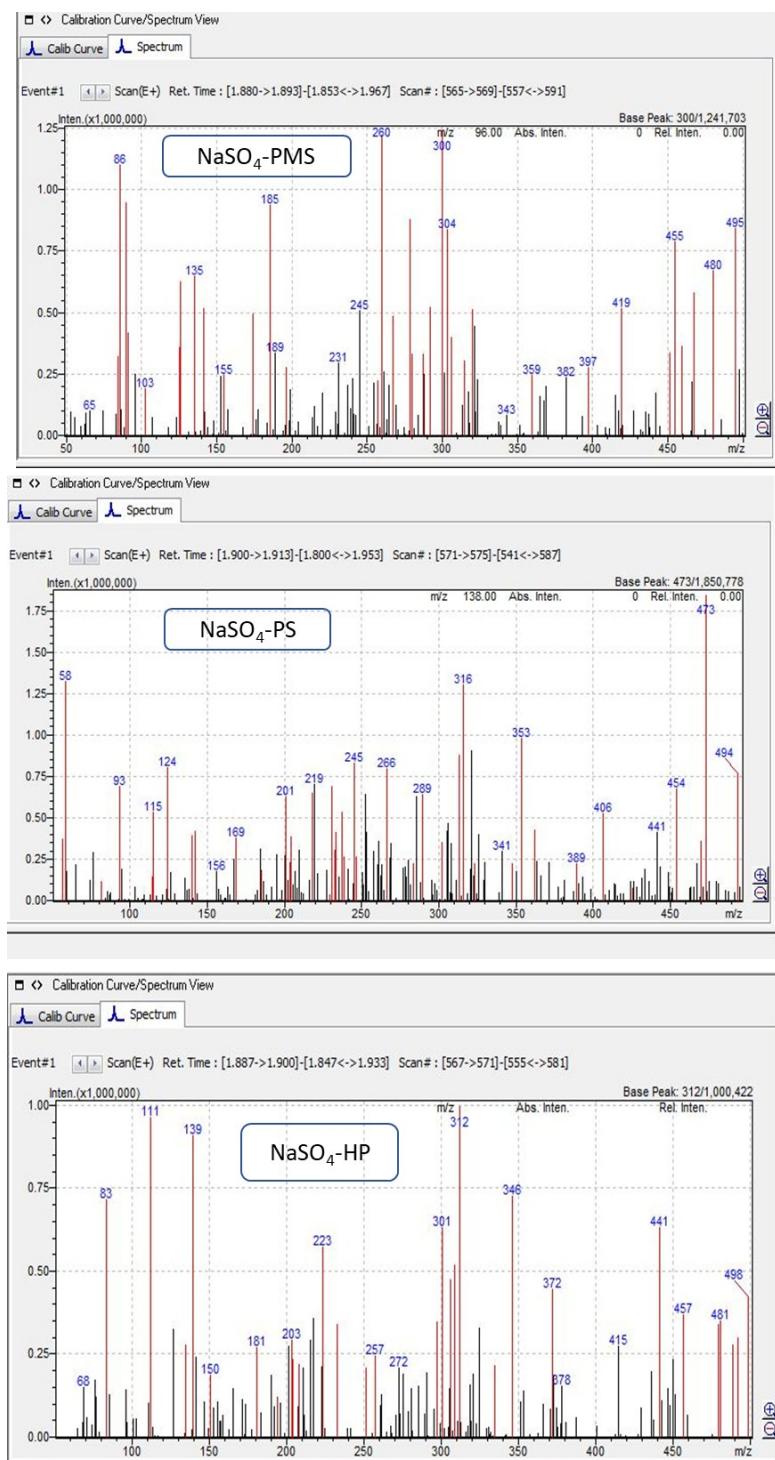
**Fig.S7** LC-MS spectra of samples obtained using EC in the presence of PMS, PS, and H<sub>2</sub>O<sub>2</sub>. Conditions: C<sub>ATL</sub> = 2.5 mg L<sup>-1</sup>, C<sub>NaCO<sub>3</sub></sub> = 1000 mg L<sup>-1</sup>, C<sub>Oxidant</sub> = 0.15 mM, initial solution pH<sub>i</sub>

= 7, and 60 min electrolysis.



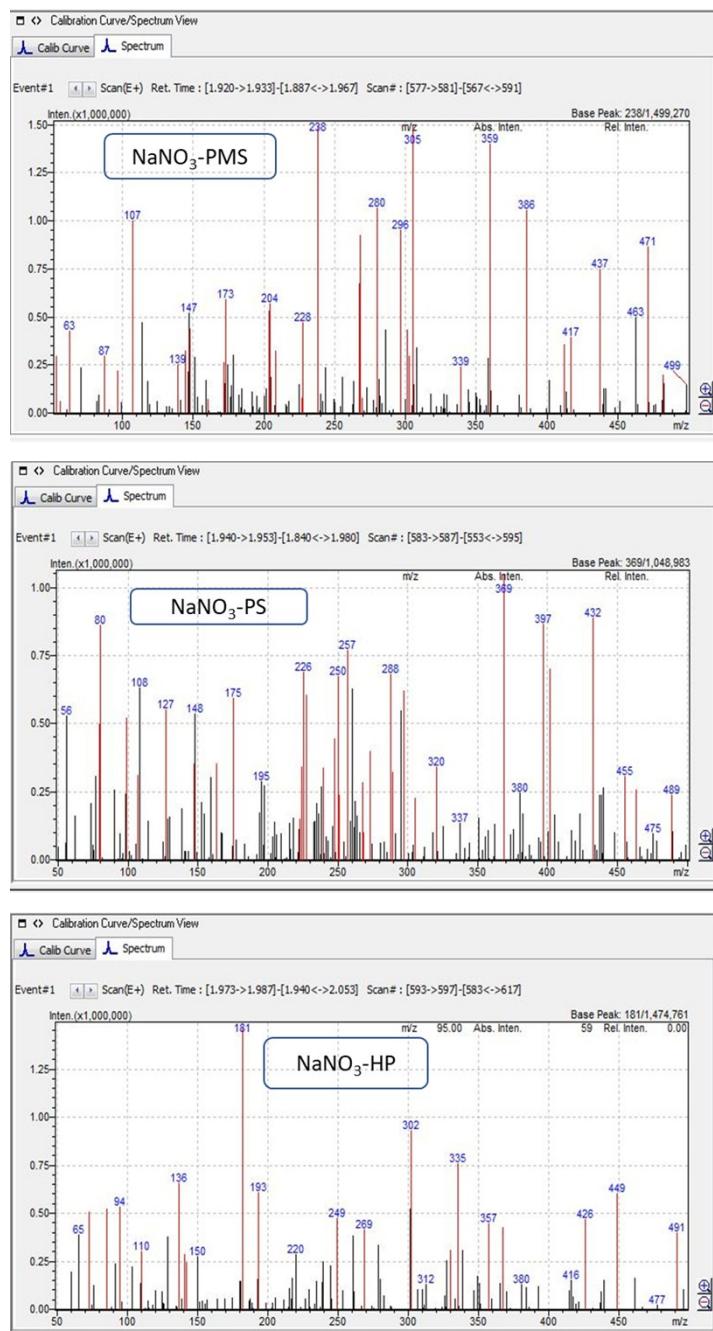
**Fig. S8** LC-MS spectra of samples obtained using EC in the presence of PMS, PS, and  $\text{H}_2\text{O}_2$ . Conditions:  $C_{\text{ATL}} = 2.5 \text{ mg L}^{-1}$ ,  $C_{\text{NaHCO}_3} = 1000 \text{ mg L}^{-1}$ ,  $C_{\text{Oxidant}} = 0.15 \text{ mM}$ , initial solution

pH<sub>i</sub> = 7, and 60 min electrolysis.



**Fig. S9** LC-MS spectra of samples obtained using EC in the presence of PMS, PS, and  $\text{H}_2\text{O}_2$ . Conditions:  $C_{\text{ATL}} = 2.5 \text{ mg L}^{-1}$ ,  $C_{\text{Na}_2\text{SO}_4} = 1000 \text{ mg L}^{-1}$ ,  $C_{\text{Oxidant}} = 0.15 \text{ mM}$ , initial solution

$\text{pH}_i = 7$ , and 60 min electrolysis.



**Fig. S10** LC-MS spectra of samples obtained using EC in the presence of PMS, PS, and  $\text{H}_2\text{O}_2$ . Conditions:  $C_{\text{ATL}} = 2.5 \text{ mg L}^{-1}$ ,  $C_{\text{NaNO}_3} = 1000 \text{ mg L}^{-1}$ ,  $C_{\text{Oxidant}} = 0.15 \text{ mM}$ , initial solution  $\text{pH}_i = 7$ , and 60 min electrolysis.