

## Supplementary materials

**Table S1. Characteristics of PVA.**

| Chemical structure  | Molecular formula                              | Relative molecular mass | Melting point | Degree of Polymerization |
|---|--|-------------------------|---------------|--------------------------|
| The chemical structure shows a polymer repeat unit consisting of two carbon atoms connected by a single bond. The first carbon is bonded to a hydroxyl group (-OH) and the second carbon is bonded to the next unit in the chain. The subscript 'n' indicates the polymer chain length. | (C <sub>2</sub> H <sub>4</sub> O) <sub>n</sub> | 95000 Da                | 230°C         | 1750±50                  |

**Table S2. Factors and coded levels of RSM**

| Factors         | units                 | coded levels |           |           |
|-----------------|-----------------------|--------------|-----------|-----------|
|                 |                       | -1           | 0         | 1         |
| pH              |                       | 6            | 7         | 8         |
| current density | (mA/cm <sup>2</sup> ) | 0.5          | 1         | 1.5       |
| electrode type  |                       | 1 (Fe/Al)    | 2 (Fe/Fe) | 3 (Al/Fe) |

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**Table S3. Experimental design and response results of RSM.**

| Run | Initial pH | Current density(mA/cm <sup>2</sup> ) | Electrode type | Actual removal efficiency (%) |
|-----|------------|--------------------------------------|----------------|-------------------------------|
| 1   | 0          | 0                                    | 0              | 98.65                         |
| 2   | 0          | 0                                    | -1             | 37.87                         |
| 3   | 1          | 0                                    | 0              | 94.81                         |
| 4   | 0          | 1                                    | 0              | 99.49                         |
| 5   | 0          | 0                                    | -1             | 30.12                         |
| 6   | -1         | 1                                    | 1              | 25.07                         |
| 7   | 0          | -1                                   | 0              | 88.54                         |
| 8   | 1          | 1                                    | 1              | 55.91                         |
| 9   | -1         | 1                                    | -1             | 20.03                         |
| 10  | -1         | -1                                   | 1              | 17.11                         |
| 11  | 1          | 1                                    | -1             | 30.01                         |
| 12  | -1         | 0                                    | 0              | 76.69                         |
| 13  | 0          | 0                                    | 0              | 96.23                         |
| 14  | 1          | -1                                   | 1              | 30.78                         |
| 15  | -1         | -1                                   | -1             | 15.81                         |
| 16  | 0          | 0                                    | 0              | 93.47                         |
| 17  | 0          | 0                                    | 0              | 99.89                         |
| 18  | 1          | -1                                   | -1             | 21.97                         |
| 19  | 0          | 0                                    | 0              | 90.34                         |
| 20  | 0          | 0                                    | 0              | 91.28                         |

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**Table S4. ANOVA for the regression response surface model.**

| Source            | Squares  | df | Square  | Value  | Prob > F |                 |
|-------------------|----------|----|---------|--------|----------|-----------------|
| Model             | 22370.32 | 9  | 2485.59 | 226.59 | < 0.0001 | significant     |
| A-initial pH      | 620.47   | 1  | 620.47  | 56.56  | < 0.0001 | significant     |
| B-current density | 316.97   | 1  | 316.97  | 28.9   | 0.0003   |                 |
| C-electrode type  | 238.14   | 1  | 238.14  | 21.71  | 0.0009   |                 |
| AB                | 55.07    | 1  | 55.07   | 5.02   | 0.0489   |                 |
| AC                | 100.61   | 1  | 100.61  | 9.17   | 0.0127   |                 |
| BC                | 54.24    | 1  | 54.24   | 4.94   | 0.0504   |                 |
| A <sup>2</sup>    | 177.5    | 1  | 177.5   | 16.18  | 0.0024   |                 |
| B <sup>2</sup>    | 0.15     | 1  | 0.15    | 0.013  | 0.9102   |                 |
| C <sup>2</sup>    | 9830.52  | 1  | 9830.52 | 896.18 | < 0.0001 | significant     |
| Residual          | 109.69   | 10 | 10.97   |        |          |                 |
| Lack of Fit       | 33.06    | 5  | 6.61    | 0.43   | 0.8113   | not significant |
| Pure Error        | 76.64    | 5  | 15.33   |        |          |                 |
| Cor Total         | 22480.01 | 19 |         |        |          |                 |

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**Table S5. Variation in PVA molecular weight with reaction time by GPC**

| Sample             | Mn    | Mw    | Mp    | Mz     | Polydispersity |
|--------------------|-------|-------|-------|--------|----------------|
| 1(The initial PVA) | 43630 | 84670 | 75833 | 136384 | 1.940623       |
| 2(10 min)          | 23470 | 48464 | 44488 | 77165  | 2.064892       |
| 3(30 min)          | 14791 | 19942 | 15951 | 26284  | 1.348275       |
| 4(60 min)          | 718   | 747   | 744   | 775    | 1.039961       |

Mw: weight-average molecular weight; Mn: number-average molecular weight; Mw/Mn: polymer dispersity index; Mz: z-average molecular weight; Mp: peak-position molecular weight; Mv: viscosity-average molecular weight. Sample 1, 2, 3, 4: four samples with different molecular weight of PVA.

| Methods  | Conditions                                | Results  | Reference    |
|--|---|--|--------------|
| Photoelectrochemical oxidation                 | PVA: 50 mg/L; pH=3; 120 min;              | PVA removal: 77.8% (Anode), 29.4% (Cathode); the specific energy consumption: 8.4 kWh/kg (Anode); 17.4kWh/kg (Cathode)   | <sup>1</sup> |
| Catalytic ozonation (CMA/O <sub>3</sub> )      | PVA: 20 mg/L; pH=7; 15 min; pH=10; 10 min | PVA removal: 97.8% at pH=7; 99.3% at pH=10   | <sup>2</sup> |
| Electrocoagulation (Fe/Al)                     | PVA:100 mg/L; pH=6.5; 120 min             | PVA removal: 77%; The specific energy consumption :15.7 kWh/kg   | <sup>3</sup> |
| Electrocoagulation (steel/ graphite rod)       | PVA: 200 mg/L; pH=7; 60 min;              | PVA removal: 93.94%; energy consumption: 2.27 kWh/m <sup>3</sup>   | <sup>4</sup> |
| Photocatalysis (P-25 TiO <sub>2</sub> and ZnO) | PVA: 20 mg/L; pH=5, 9; 150 min            | PVA removal: 54% (P-25 TiO <sub>2</sub> ) and 74% (ZnO) at pH=9  | <sup>5</sup> |
| Ozone oxidation                                | PVA: 20 g/L; pH=9; 240 min;               | PVA removal: 99%   | <sup>6</sup> |
| APC-EC (Fe/Fe)                                 | PVA: 150 mg/L; pH=7; 60 min;              | PVA removal: 99.85%; energy consumption: 0.059 kWh/m <sup>3</sup> ; theoretical electrode consumption: 0.208 kg/m <sup>3</sup> ; electrode consumption: 0.105g | This work    |

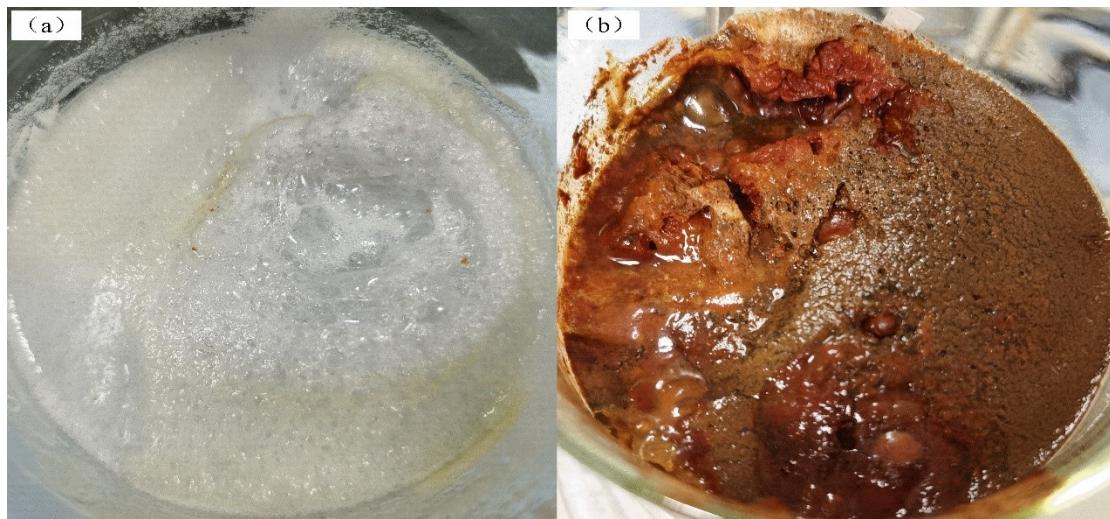
**Table S6. PVA removal methods in previous studies.**

1. K.Y. Huang, C.T. Wang, W.L. Chou and C.M. Shu, International Journal of Photoenergy, 2015, **2015**, 623492.
2. Z. Yan, J. Zhu, X. Hua, D. Liang, D. Dong, Z. Guo, N. Zheng and L. Zhang, Journal of Cleaner Production, 2020, **272**, 122856.
3. W.L. Chou, C.T. Wang and K.Y. Huang, Desalination, 2010, **251**, 12-19.
4. Z. Wang, X. Teng, M. Xie, X. Cheng and J. Li, Journal, 2020, **31**, 2864-2870.
5. A. R. Nunes, A. O. Moura and A. G. S. Prado, J. Therm. Anal. Calorim., 2011, **106**, 445-452.
6. G. Zhu, F. Zhang, P. Jiang and M. Ge, Journal of the Textile Institute, 2021, **112**, 117-122.

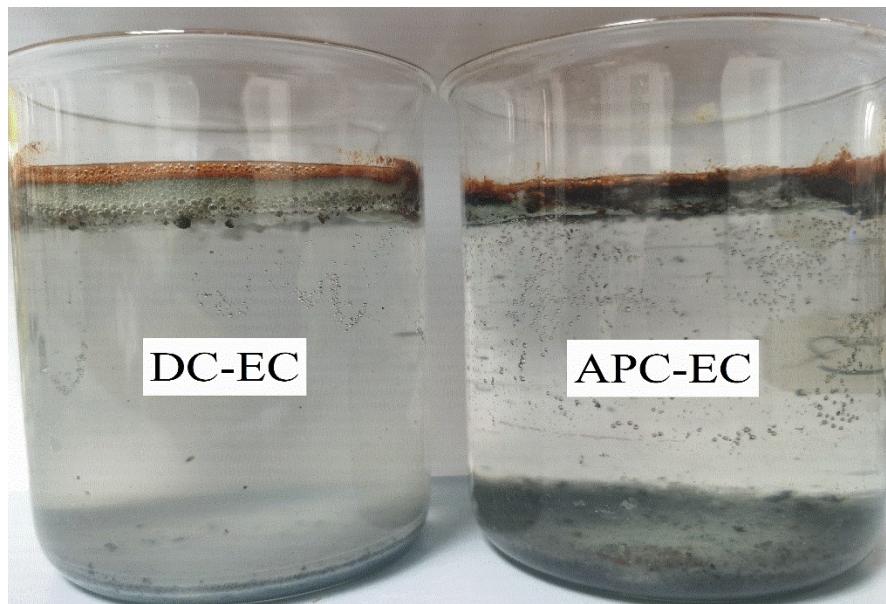
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**Table S7. Two-kind EC method performance comparison analysis**

| Elements   | DC-EC  | APC-EC |
|--|--------|--------|
| Removal efficiency (%)                                 | 92.82% | 99.73% |
| Energy consumption (kWh/m <sup>3</sup> )               | 0.480  | 0.049  |
| Theoretical electrode consumption (kg/m <sup>3</sup> ) | 0.237  | 0.174  |
| Actual electrode consumption (g)                       | 0.190  | 0.105  |
| Sludge weight (g)                                      | 0.1193 | 0.0674 |
| Electrode stability (%)                                | 83.27% | 95.28% |
| Current efficiency (%)                                 | 62.37% | 99.05% |



**Fig. S1.** The images of flocs after the EC process for (a) Al and (b) Fe electrodes.



**Fig. S2.** The images of flocs after the DC-EC and APC-EC processes.