Pengembangan dan Kajian Mekanistik Sensor Elektrokimia Berbasis Hybrid Multilayer Elektroda Pasta Karbon Biochar Ampas Teh untuk Analisis Tartrazin dalam Produk Minuman

Program Riset ITB 2026 – Skema Riset Unggulan ITB

Ria Sri Rahayu[1]*, Ananda Mayusra[1], Achmad Rochliadi[1], Nurhayati[1]

[1] Program Studi Kimia, FMIPA, Institut Teknologi Bandung · * penulis korespondensi

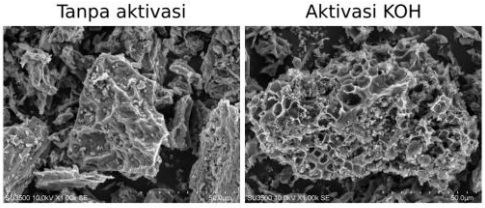
Abstract

Ampas teh diubah menjadi biochar dan diaktivasi dengan KOH (1:3 b/b, 550 °C). Luas permukaan BET naik dari 140 menjadi 1172 m² g^{-1}, dan 89% volume pori sudah terisi pada p/p_0 = 0,1 sehingga material bersifat mikropori. Biochar dicampurkan ke dalam pasta karbon (EPK), lalu dilapisi grafena oksida tereduksi secara elektrokimia (ErGO) dan kitosan (CS).
Lima konfigurasi elektroda dibandingkan dengan probe $[Fe(CN)_6]^{3-/4-}$. Biochar 8% b/b terutama menurunkan tahanan transfer muatan (3874 → 448 Ω), sedangkan ErGO menggandakan luas elektroaktif semu (0,052 → 0,112 cm²).
Pada PBS pH 7 dengan akumulasi 30 s, CS/ErGO/BC/EPK memberikan respons DPV linear pada 0,5–10 µM (R^2 0,998). LOD 0,56 µM dan LOQ 1,7 µM. RSD keterulangan 1,3–4,9% (n = 6) dan RSD rerata tiga elektroda 3,8%.

Keyword: tartrazin; biochar; ampas teh; elektroda pasta karbon; ErGO; kitosan

Introduction

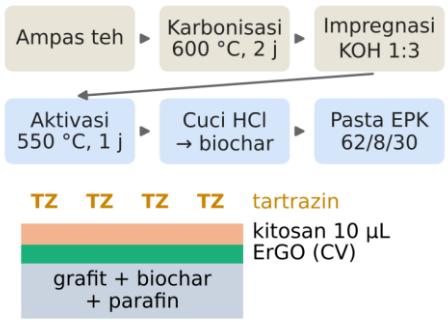
Tartrazin (E102) adalah pewarna azo sintetis yang banyak dipakai pada minuman ringan, sirup dan permen. Penggunaannya dibatasi; di Indonesia batas maksimum untuk minuman berbasis air berperisa adalah 70 mg kg^{-1} (Peraturan BPOM No. 11 Tahun 2019).
Pengujian rutin umumnya memakai HPLC atau spektrofotometri UV–Vis. Kedua metode andal tetapi membutuhkan laboratorium pusat, dan spektrofotometri mudah terganggu bila ada beberapa pewarna kuning sekaligus.
Voltammetri menjadi alternatif karena tartrazin teroksidasi pada elektroda karbon. Kebanyakan sensor tartrazin memakai pemodifikasi sintetis seperti nanopartikel logam, MOF atau nanotube karbon, dan jarang menunjukkan komponen mana yang bertanggung jawab atas perubahan respons.
Biochar dari limbah biomassa murah dan porositasnya dapat diatur melalui aktivasi. Sejauh penelusuran kami, biochar ampas teh belum pernah dipakai untuk sensor tartrazin.
Tujuan: (i) mengaitkan sifat tekstur biochar dengan kinerja pasta, (ii) mengidentifikasi peran tiap lapisan (BC, ErGO, CS) dengan probe redoks, dan (iii) menentukan kinerja analitik elektroda akhir untuk tartrazin.



Picture 1. SEM biochar tanpa aktivasi (kiri) dan teraktivasi KOH (kanan)

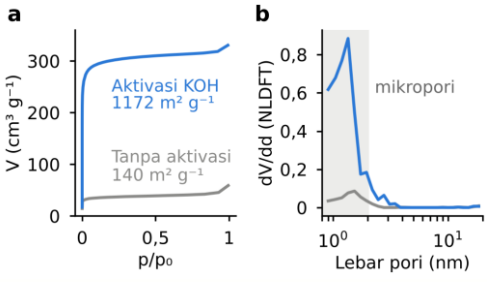
Research Method

Biochar. Ampas teh dikarbonisasi pada 600 °C (2 jam), diimpregnasi KOH (1:3 b/b), dipanaskan pada 550 °C (60 menit, krus tertutup, udara statis), dicuci HCl 1 M hingga netral, lalu dikarakterisasi dengan adsorpsi N_2 (BET, t-plot, NLDFT), SEM-EDS dan FTIR.
Elektroda. Pasta grafit/biochar/parafin (62/8/30 % b/b) dimasukkan ke tabung kaca (Ø 1,5 mm). GO (5 µL, 1 mg mL^{-1}) diteteskan lalu direduksi dengan CV (−1,2 s.d. +0,6 V, Na_2SO_4 0,1 M). Kitosan 0,5% b/v diteteskan di atasnya.



Picture 2. Tahapan pembuatan biochar dan elektroda CS/ErGO/BC/EPK

Pengukuran. CV probe dan EIS: PalmSens4 (PSTrace 5.6); DPV tartrazin: eDAQ EA163 (EChem 2.1.16). Sel tiga elektroda yang sama: Ag/AgCl (KCl 3 M) dan kawat Pt. Probe redoks: $[Fe(CN)_6]^{3-/4-}$ 5 mM dalam KCl 0,1 M (CV 100 mV s^{-1}; EIS 100 kHz–0,1 Hz). Luas elektroaktif semu dihitung dengan persamaan Randles–Ševčík.
Optimasi. Kandungan biochar 0–10% b/b; pH 3–7; volume kitosan 2–10 µL; waktu akumulasi 0–180 s.
Validasi. Kalibrasi DPV 0,5–10 µM (blanko n = 10, sesi sama); LOD/LOQ 3,3σ/S dan 10σ/S; uji Mandel; keterulangan (n = 6); reprodusibilitas (3 × 3); ANOVA (α = 0,05).

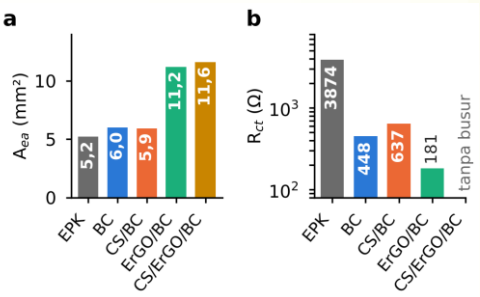


Picture 3. (a) Isoterm N_2 dan (b) pori NLDFT; biru = aktivasi KOH, abu-abu = tanpa aktivasi

1172	0,5–10	0,56	3,8%
m² g^{-1} BET	µM linear	µM LOD	RSD 3 elektroda

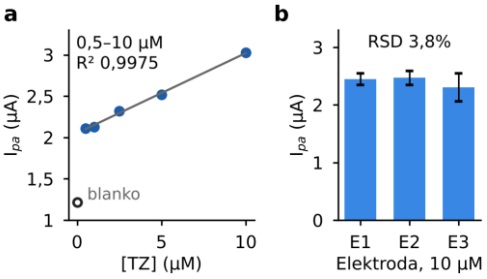
Discussion & Result

Karakter biochar. Kedua isoterm bertipe I. Aktivasi KOH menaikkan luas BET dari 140 menjadi 1172 m² g^{-1} dan volume mikropori dari 0,043 menjadi 0,385 cm^3 g^{-1}. Pita karbonat FTIR (1420, 874, 712 cm^{-1}) hilang setelah aktivasi, dan rasio O/C (EDS, semikuantitatif) turun dari 0,21 menjadi 0,16.
Peran tiap lapisan. Di antara kadar 0–10% b/b, biochar 8% memberi Rct terendah (0,48 kΩ). Biochar terutama menurunkan Rct (3874 → 448 Ω), sedangkan luas elektroaktif hanya sedikit naik. ErGO menurunkan Rct lebih lanjut (181 Ω) dan menggandakan luas elektroaktif. Kitosan menghambat probe anionik, tetapi sinyal tartrazin naik seiring volume kitosan (0,95 → 3,01 µA).



Picture 4. (a) Luas elektroaktif semu dan (b) Rct; CS/ErGO/BC tanpa busur Rct

Kinerja analitik. Respons linear 0,5–10 µM (R^2 0,9975; uji Mandel p = 0,86). LOD estimasi 0,56 µM; rentang kuantitatif 1,7–10 µM. RSD keterulangan 4,9% (10 µM); RSD rerata 3 elektroda 3,8% (ANOVA p = 0,46).



Picture 5. (a) Kalibrasi tartrazin 0,5–10 µM; (b) reprodusibilitas 3 elektroda

Conclusion

Biochar teraktivasi KOH (1172 m² g^{-1}) menurunkan Rct pasta karbon, ErGO menggandakan luas elektroaktif, dan sinyal tartrazin naik seiring jumlah kitosan.
Dalam larutan standar, respons DPV linear pada 0,5–10 µM dengan LOD estimasi 0,56 µM dan presisi yang baik (RSD ≤ 4,9%), sehingga berpotensi untuk penapisan tartrazin dalam minuman berwarna setelah pengenceran.
Biochar ampas teh adalah pemodifikasi elektroda yang murah dan bebas logam dari limbah pangan.

Development and Mechanistic Study of an Electrochemical Sensor Based on a Hybrid Multilayer Spent-Tea Biochar Carbon Paste Electrode for Tartrazine in Beverages

ITB Research Programme 2026 – Riset Unggulan ITB Scheme

Ria Sri Rahayu[1]*, Ananda Mayusra[1], Achmad Rochliadi[1], Nurhayati[1]

[1] Chemistry Study Program, FMIPA, Institut Teknologi Bandung · * corresponding author

Abstract

Spent tea leaves were carbonised and activated with KOH (1:3 w/w, 550 °C). The BET area rose from 140 to 1172 m² g⁻¹, and 89% of the pore volume was filled at p/p_0 = 0.1, showing a microporous carbon. The biochar was mixed into a carbon paste electrode (CPE), which was coated with electrochemically reduced graphene oxide (ErGO) and chitosan (CS).

Five electrode configurations were compared with the $[Fe(CN)_6]^{3-/4-}$ probe. Biochar (8 wt%) mainly lowered the charge-transfer resistance (3874 → 448 Ω), whereas ErGO doubled the apparent electroactive area (0.052 → 0.112 cm²).

In PBS pH 7 with 30 s accumulation, the DPV response of CS/ErGO/BC/CPE was linear from 0.5 to 10 µM (R^2 0.998), with estimated LOD and LOQ of 0.56 and 1.7 µM. Repeatability RSD was 1.3–4.9% (n = 6) and the RSD of three electrode means 3.8%.

Keywords: tartrazine; biochar; spent tea; carbon paste electrode; ErGO; chitosan

Introduction

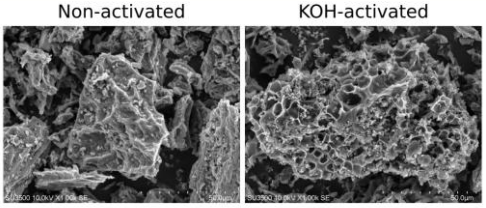
Tartrazine (E102) is a synthetic azo dye widely used in soft drinks, syrups and confectionery. Its use is regulated; in Indonesia the maximum level in water-based flavoured drinks is 70 mg kg⁻¹ (BPOM Regulation No. 11/2019).

Routine control relies on HPLC or UV–Vis spectrophotometry. Both are reliable but need a central laboratory, and spectrophotometry is biased when several yellow dyes are present.

Voltammetry is an alternative because tartrazine is oxidised at carbon electrodes. Most tartrazine sensors use synthetic modifiers such as metal nanoparticles, MOFs or carbon nanotubes, and few show which component is responsible for which change in the response.

Biochar from biomass waste is inexpensive, and its porosity can be tuned by activation. To our knowledge, spent-tea biochar has not been used in a tartrazine sensor.

Aims: (i) relate the texture of the biochar to the behaviour of the paste, (ii) identify the role of each layer (BC, ErGO, CS) with a redox probe, and (iii) establish the analytical performance of the final electrode for tartrazine.

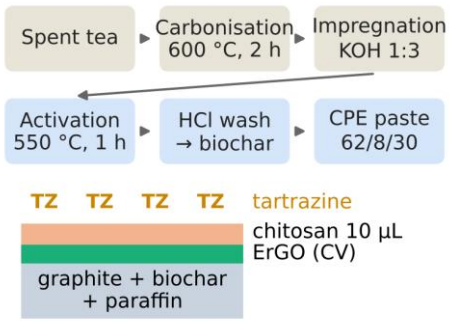


Picture 1. SEM of non-activated (left) and KOH-activated (right) biochar

Research Method

Biochar. Spent tea was carbonised at 600 °C (2 h), impregnated with KOH (1:3 w/w), heated at 550 °C (60 min, covered crucible, static air), washed with 1 M HCl to neutral, and characterised by N_2 sorption (BET, t-plot, NLDFT), SEM-EDS and FTIR.

Electrode. A graphite/biochar/paraffin paste (62/8/30 wt%) was packed into a glass tube (Ø 1.5 mm). GO (5 µL, 1 mg mL⁻¹) was drop-cast and reduced by CV (−1.2 to +0.6 V, 0.1 M Na_2SO_4). Chitosan (0.5% w/v) was drop-cast on top.

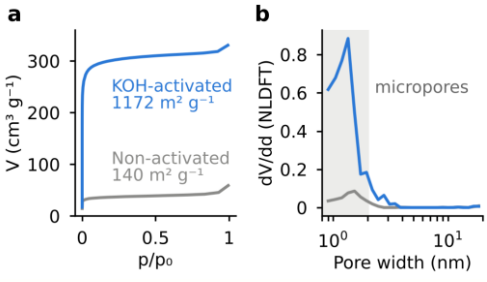


Picture 2. Preparation of the biochar and the CS/ErGO/BC/CPE

Measurements. Probe CV and EIS: PalmSens4 (PSTrace 5.6); tartrazine DPV: eDAQ EA163 (EChem 2.1.16). Same three-electrode cell: Ag/AgCl (3 M KCl) and Pt wire. Redox probe: 5 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl (CV 100 mV s⁻¹; EIS 100 kHz–0.1 Hz). Apparent electroactive area from the Randles–Ševčík equation.

Optimisation. Biochar content 0–10 wt%; pH 3–7; chitosan volume 2–10 µL; accumulation time 0–180 s.

Validation. DPV calibration 0.5–10 µM (blank n = 10, same session); LOD/LOQ 3.3σ/S and 10σ/S; Mandel test; repeatability (n = 6); reproducibility (3 × 3); ANOVA (α = 0.05).



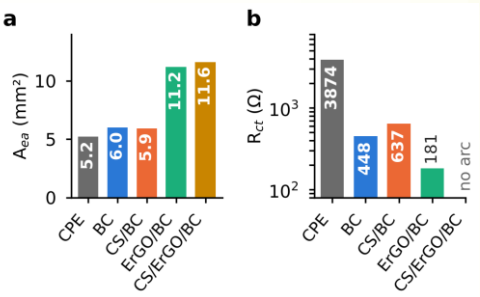
Picture 3. (a) N_2 isotherms, (b) NLDFT pores; blue = KOH-activated, grey = non-activated

1172 m² g⁻¹ BET | **0.5–10** µM linear | **0.56** µM est. LOD | **3.8%** RSD, 3 electrodes

Discussion & Result

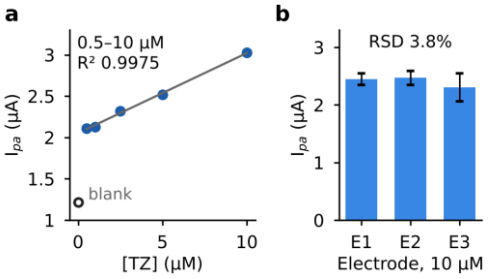
Biochar. Both isotherms are Type I. KOH activation raised the BET area from 140 to 1172 m² g⁻¹ and the micropore volume from 0.043 to 0.385 cm³ g⁻¹. FTIR carbonate bands (1420, 874, 712 cm⁻¹) disappeared after activation, and the atomic O/C ratio (EDS, semi-quantitative) fell from 0.21 to 0.16.

Role of each layer. Among 0–10 wt%, 8 wt% biochar gave the lowest Rct (0.48 kΩ). Biochar mainly lowered Rct (3874 → 448 Ω), while the electroactive area rose only slightly. ErGO lowered Rct further (181 Ω) and doubled the electroactive area. Chitosan hindered the anionic probe, but the tartrazine signal increased with chitosan volume (0.95 → 3.01 µA).



Picture 4. (a) Apparent electroactive area and (b) Rct; no arc for CS/ErGO/BC

Analytical performance. Linear from 0.5 to 10 µM (R^2 0.9975; Mandel test p = 0.86). Estimated LOD 0.56 µM; quantitative range 1.7–10 µM. Repeatability RSD 4.9% (10 µM); RSD of three electrode means 3.8% (ANOVA p = 0.46).



Picture 5. (a) Tartrazine calibration, 0.5–10 µM; (b) reproducibility, 3 electrodes

Conclusion

KOH-activated spent-tea biochar (1172 m² g⁻¹) lowered the Rct of the carbon paste, ErGO doubled the electroactive area, and the tartrazine signal increased with chitosan loading.

In standard solutions the DPV response was linear from 0.5 to 10 µM with an estimated LOD of 0.56 µM and good precision (RSD ≤ 4.9%), giving potential for screening tartrazine in coloured beverages after dilution.

Spent-tea biochar is a low-cost, metal-free electrode modifier made from food waste.