# INTISARI

Dengan melimpahnya jumlah serta kandungan senyawa organik yang tinggi, *vinasse* sangat berpotensi dimanfaatkan sebagai bahan baku biogas. Akan tetapi, kandungan *Total Chemical Oxygen Demand* (TCOD) yang terlalu tinggi dalam limbah tersebut dapat menghambat proses pencernaan *anaerob* (*anaerobic digestion* disingkat AD). Oleh karena itu, *pretreatment* perlu dilakukan untuk menurunkan TCOD-nya sebelum *vinasse* digunakan sebagai bahan baku biogas. Pada penelitian ini, elektrokoagulasi (*electrocoagulation* disingkat EC) dipilih sebagai metode *pretreatment* karena (1) dapat menurunkan TCOD, (2) mudah dioperasikan, (3) peralatan sederhana, (4) lebih efektif dan efisien dibandingkan koagulasi kimia, (5) dihasilkan gas hidrogen yang membantu pemisahan polutan melalui proses flotasi dan dapat disimpan sebagai sumber energi. Tujuan penelitian ini adalah (1) mempelajari pengaruh variabel input EC terhadap perubahan kandungan kimia dalam *vinasse*, (2) mempelajari pengaruh *pretreatment* EC terhadap peningkatan produksi biogas dari *vinasse*, (3) membuat model yang dapat merepresentasikan proses-proses yang terjadi pada EC dan dapat dipakai untuk memprediksi karakteristik *vinasse* hasil EC, (4) menyusun model mekanistik yang dapat dipakai untuk memprediksi unjuk kerja produksi biogas dari berbagai karakteristik *vinasse* hasil EC. Penelitian ini lebih difokuskan pada studi proses EC.

*Vinasse* diperoleh dari salah satu industri bioetanol berbahan baku *molasse* di Indonesia yang mengandung TCOD 100.160,7-112.948,5 mg/L, Fe total 28,63-109,59 mg/L, sulfat 615,62-8.338,85 mg/L and fenol total <0,1 mg/L. Variabel input EC yang dipelajari meliputi pH umpan, tegangan listrik, arus listrik dan kecepatan pengadukan. Proses EC dilakukan secara *batch* menggunakan gelas beaker volume 1000 mL (IWAKI pyrex, dengan tinggi 1,52 dm, diameter luar 1,1 dm dan diameter dalam 1,05 dm) sebagai reaktor EC skala laboratorium. Elektroda besi (Fe) dipilih karena murah dan dapat meningkatkan kadar Fe dalam *vinasse* di akhir proses. Proses EC dijalankan dengan volume *vinasse* 1 $dm^3$ (tanpa pengenceran), dimensi elektroda aktif dengan panjang 0,95 dm, lebar 0,3 dm, tebal 0,03 dm ($A_e$=0,64 $dm^2$), jarak antar elektroda 0,55 dm, kecepatan pengadukan 200-500 rpm, pH umpan 4,35-6, tegangan listrik 7,5-12,5 V dan arus listrik 2,5-3,5 A. Parameter yang terukur selama proses EC adalah perubahan pH cairan, suhu cairan, arus listrik, tegangan listrik, volume cairan, konsentrasi TCOD, konsentrasi Fe total, massa *scum* dan massa *sludge*. Proses AD dilakukan secara *batch* menggunakan digester skala laboratorium 400 mL dengan volume aktif 300 mL. Umpan digester memiliki rasio *vinasse*/inokulum=3,5/1 (gTCOD/gVS). Parameter yang terukur selama proses AD adalah perubahan pH cairan, konsentrasi TCOD, konsentrasi *volatile fatty acid* (VFA), jumlah mikroba total, volume biogas dan persentase metan di dalam biogas.

Hasil penelitian menunjukkan bahwa selama proses EC, pH cairan mengalami kenaikan karena ion $OH^-$ diproduksi selama reaksi reduksi pada katoda. Suhu cairan mengalami kenaikan karena suplai arus yang terus-menerus. Volume cairan mengalami penurunan karena air tereduksi menjadi $OH^-$ dan gas $H_2$, air menguap (evaporasi) pada suhu yang tinggi dan air terbawa saat pembentukan *scum*. Peningkatan variabel input pH umpan dari 4,35 sampai 6 dapat meningkatkan efisiensi pengurangan massa TCOD dari 9,77 sampai 27,34% untuk lama proses 1 jam. Pada kondisi pH netral, koagulan $Fe(OH)_2$ mudah terbentuk sehingga laju penurunan TCOD lebih cepat pada pH netral dibandingkan pH asam.

Peningkatan tegangan listrik dari 7,5 ke 12,5 V dapat meningkatkan efisiensi pengurangan massa TCOD dari 18,91 ke 48,59% untuk lama proses 1 jam. Selanjutnya, peningkatan arus listrik dari 2,5 ke 3,5 A dapat meningkatkan efisiensi pengurangan massa TCOD dari 39,83 ke 71,96% untuk lama proses 8 jam. Selain itu, peningkatan arus listrik dari 2,5 ke 3,5 A dapat meningkatkan efisiensi pengurangan massa sulfat dari 17,71 ke 65,20%. Semakin tinggi arus listrik, semakin banyak ion $Fe^{2+}$ yang dihasilkan dari reaksi oksidasi sehingga dosis koagulan $Fe(OH)_2$ yang disuplai ke dalam sistem semakin banyak, akibatnya proses adsorpsi polutan oleh koagulan lebih mudah terjadi. Sementara itu, kandungan fenol tidak diukur karena *raw vinasse* sudah mengandung fenol total yang sangat sedikit (<0,1 mg/L). Kandungan Fe total dalam limbah mengalami peningkatan setelah melalui proses EC. Tujuh model mekanistik (Model EC 1-7) disusun berdasarkan mekanisme reaksi yang terjadi selama proses EC. Model EC 7 merupakan model paling lengkap karena memiliki lima konstanta kinetik yang bebas dari pengaruh konsentrasi TCOD, konsentrasi Fe total, *current density*, luas permukaan aktif elektroda, volume cairan, suhu cairan, pH cairan dan kecepatan pengadukan. Model EC 7 berhasil diaplikasikan dengan kecocokan visual yang bagus. Nilai konstanta-konstanta kinetik pada Model EC 7 berhasil diperoleh setelah Model EC 7 digunakan untuk memprediksi 194 data proses EC.

*Vinasse* keluaran proses EC pada varibel input arus listrik 2,5-3,5 A dengan waktu proses 8 jam diumpankan ke dalam sistem AD sebagai bahan baku biogas. *Sludge* dari reaktor biogas aktif berbahan baku kotoran sapi digunakan sebagai inokulum. Variabel input proses AD adalah konsentrasi TCOD (12,90-85,10 g/L) dan konsentrasi Fe total (0,012-0,94 g/L) dalam substrat. Penurunan konsentrasi TCOD dari 85,10 ke 12,90 g/L dapat meningkatkan *yield* biogas dari 9,82 ke 102,08 mL biogas/g TCOD umpan (*Standard Temperature and Pressure condition*). Untuk AD dengan konsentrasi Fe total <0,1 g/L, konsentrasi VFA >12 g asam asetat/L tidak disarankan karena dapat menghambat laju produksi biogas. Ketika konsentrasi Fe total di dalam substrat tinggi (0,65-0,94 g Fe/L), konsentrasi VFA hingga 22 g asam asetat/L tidak menghambat proses pembentukan biogas. Keberadaan Fe berhasil mengurangi efek penghambatan oleh tingginya konsentrasi VFA. *Yield* metan yang dihasilkan dengan *pretreatment* EC sebesar 47,51 mL $CH_4$/g TCOD umpan (87,46 mL $CH_4$/g TCOD yang hilang), sedangkan tanpa *pretreatment* sebesar 0,86 mL $CH_4$/g TCOD umpan (4,10 mL $CH_4$/g TCOD yang hilang). Model AD berhasil disusun dan diaplikasikan dengan kecocokan visual yang cukup baik. Nilai tiga belas konstanta kinetik dari Model AD berhasil diperoleh setelah Model AD digunakan untuk memprediksi 351 data proses AD.

Kesimpulan yang dapat diambil dari penelitian ini adalah (1) EC berhasil menurunkan TCOD dan sulfat, tetapi meningkatkan kandungan Fe total, (2) AD dari *vinasse* yang telah diolah melalui proses EC menghasilkan metan dengan jumlah *yield* yang jauh lebih besar dibandingkan dari *raw vinasse*, (3) Model EC 7 dengan lima konstanta kinetik berhasil disusun dan digunakan untuk memprediksi karakteristik *vinasse* hasil EC dan (4) Model AD dengan tiga belas konstanta kinetik berhasil disusun dan digunakan untuk memprediksi unjuk kerja produksi biogas. Model-model tersebut diharapkan bisa dipakai untuk rancangan sistem pemrosesan skala besar.

**Kata Kunci:** *Biogas, Elektrokoagulasi, Fe, Model Mekanistik, TCOD, Vinasse*

# ***ABSTRACT***

*By its abundant amount and high organic compounds, vinasse has the potential to be used as a biogas feedstock. However, the too high Total Chemical Oxygen Demand (TCOD) concentration in the waste can inhibit the anaerobic digestion (AD) process. Therefore, a pretreatment need to be carried out to reduce its TCOD concentration before the vinasse is used as the biogas feedstock. In this study, electrocoagulation (EC) was chosen as a pretreatment method because (1) it can reduce the TCOD, (2) it is easy to operate, (3) it has simple equipments, (4) it is more effective and efficient than the chemical coagulation, (5) it produces hydrogen gas which helps the separation of pollutants through the flotation process and can be stored as an energy source. The aims of this study are (1) to study the effect of EC input variables on changes in chemical characteristics in vinasse, (2) to study the effect of EC as a pretreatment of AD on increasing biogas production from vinasse, (3) to create mechanistic models that can represent the processes that occur in EC and can be used to predict the vinasse characteristics after the EC process, (4) to develop a mechanistic model that can be used to predict biogas production performance from various chemical characteristics of EC-pretreated vinasse. This study is more focused on the EC process.*

*Vinasse was obtained from one of the bioethanol industries producing bioethanol from molasses in Indonesia which contains TCOD 100,160.7-112,948.5 mg/L, total Fe 28.63-109,59 mg/L, sulfate 615.62-8,338.85 mg/L and total phenol <0.1 mg/L. The EC input variables, which were studied in this study, included the intial pH, electrical voltage, electrical current and agitation speed. The EC process was carried out under a batch system using a 1000 mL-glass beaker (IWAKI pyrex, with dimention of height, outside diameter and inside diameter of 1.52 dm, 1.1 dm and 1.05 dm respectively) as a laboratory scale EC reactor. The iron electrodes (Fe) were chosen because they are cheap and can increase the total Fe content in the vinasse at the end of the EC process. The EC process was run with a vinasse volume of 1 $dm^3$ (without dilution), the active electrode dimention of length, width and thickness of 0.95 dm, 0.3 dm and 0.03 respectively (active surface area of 0.64 $dm^2$), inter-electrode distance of 0.55 dm, agitation speed of 200-500 rpm, electrical voltage of 7.5-12.5 V, initial pH of 4.35-6 and electrical current of 2.5-3.5 A. The measured parameters during the EC process were changes in solution pH, solution temperature, electrical current, electrical voltage, solution volume, TCOD concentration, total Fe concentration, scum mass and sludge mass. The AD process was carried out under a batch system using laboratory scale digesters with total volume of 400 mL and active volume of 300 mL. The AD substrates had a vinasse/inoculum ratio of 3.5/1 (g TCOD/g VS). The measured parameters during the AD process were changes in solution pH, TCOD concentration, volatile fatty acid (VFA) concentration, total microbial count, biogas volume and methane percentage in biogas.*

*The results showed that during the EC process, the solution pH increased because OH- ions were produced during the reduction reaction at cathode side. The solution temperature increased due to the continuous supply of electrical current. The solution volume decreased because the water was reduced to become $OH^-$ and $H_2$ gas, the water was evaporated at high temperature and the water was carried away during the scum formation. Increasing the initial pH from 4.35 to 6 increased the removal efficiency of TCOD mass from 9.77 to 27.34% after 1 h processing time. At neutral pH conditions, the $Fe(OH)_2$ coagulants* *were easily formed so that the rate of pollutant reduction was faster at neutral pH than at acidic pH. Increasing the electrical voltage from 7.5 to 12.5 V increased the removal efficiency of TCOD mass from 18.91 to 48.59% after 1 h processing time. Furthermore, increasing the electrical current from 2.5 to 3.5 A increased the removal efficiency of TCOD mass from 39.83 to 71.96% after 8 h processing time. In addition, increasing the electric current from 2.5 to 3.5 A increased the removal efficiency of sulfate mass from 17.71 to 65.20%. The higher the electrical current, the more the $Fe^{2+}$ ions were produced through oxidation reactions so the more the $Fe(OH)_2$ coagulant dose was supplied in the system, as consequent the adsorption process of pollutant on coagulants was easier to occur. Meanwhile, the total phenol concentration was not measured because the raw vinasse already contained very little total phenol (<0.1 mg/L). The total Fe in the vinasse increased after the waste was treated through the EC process. Seven mechanistic models (Model EC 1-7) were arranged based on the mechanism of reactions that occur during EC process. The Model EC 7 was the most complete model because it has five kinetic constants that were independent of the influence of TCOD concentration, total Fe concentration, current density, active surface electrode, solution volume, solution temperature, solution pH and agitation speed. The Model EC 7 was successfully applied with a good visual fit. The values of the kinetic constants in Model EC 7 were successfully obtained after Model EC 7 was used to predict 194 data of the EC process.*

*The EC-pretreated vinasse after EC process with 2.5-3.5 A for 8 h was fed into the AD system as a biogas feedstock. Furthermore, a sludge from an active biogas reactor treating the cow dung was used as an inoculum. The input variables for the AD process were the TCOD concentration (12.90-85.10 g/L) and the total Fe concentration (0.012-0.94 g/L) in the substrate. The decrease in TCOD concentration from 85.10 to 12.90 g/L increased the biogas yield from 9.82 to 102.08 mL biogas/g initial TCOD (Standard Temperature and Pressure condition). For AD with total Fe concentration <0.1 g/L, VFA concentration >12 g acetic acid/L was not recommended because it inhibited the rate of biogas production. When the concentration of total Fe in the substrate was high (0.65-0.94 g/L), the VFA concentration of up to 22 g acetic acid/L did not inhibit the biogas formation process. The presence of Fe succeeded in reducing the inhibitory effect by the high VFA concentration. Methane yield for AD with pretreatment of EC was 47.51 mL $CH_4$/g initial TCOD (87.46 mL $CH_4$/g removed TCOD) and without pretreatment of EC was 0.86 mL $CH_4$/g initial TCOD (4.10 mL $CH_4$/g removed TCOD). The Model AD was successfully compiled and applied with a fairly good visual fit. The value of thirteen kinetic constants from the Model AD was successfully obtained after the Model AD was used to predict 351 data of the AD process.*

*The conclusions of this study were (1) the EC succeeded in reducing the TCOD and sulfate content, but increased the total Fe content, (2) the AD from the EC-pretreated vinasse produced a much higher methane yield than that from the raw vinasse, (3) the Model EC 7 with five kinetic constants was successfully compiled and used to predict the chemical characteristics of EC effluents and (4) the Model AD with thirteen kinetic constants was successfully compiled and used to predict the performance of biogas production. These models are expected to be used for the design of large-scale processing systems*

***Keywords:*** *Biogas, Electrocoagulation, Fe, Mechanistic Model, TCOD, Vinasse*