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Electro-degradation and biological oxidation of non-biodegradable organic contaminants

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ABSTRACT

The speciality chemical process requires large volumes of water of high purity and generates equally large volumes of wastewater. The generated wastewater is complex and highly variable with respect to its nature, containing high levels of chemical oxygen demand (COD), dissolved and suspended solids, a medium to low level of biochemical oxygen demand, a considerable amount of total organic halogen and an intense colour. In the present study the actual effluent was collected from the organic industry and various experiments were conducted to reduce the pollution load and reuse treated wastewater.

The wastewater typically contains COD about 48,000 mg L^{-1}. When it was distilled, the COD of the condensate reduces to 17,000 mg L^{-1} which was subjected to electrolytic degradation and subsequently biological oxidation. The operation was continued using various microorganisms such as *Bacillus subtilis*, *Pseudomonas aeruginosa* and *Proteus vulgaris* in a batch reactor. Minimum of 80% reduction of COD was obtained in the combined process.

1. Introduction

The efficient amputations of refractory or recalcitrant compounds present in organic industrial effluents are still a major environmental challenge. Refractory or recalcitrant compounds in this context are those, which resist aerobic microbial degradation in natural environment and conventional biological treatment processes. A literature survey shows that research continues to be conducted in the areas of chemical and combined chemical biological treatments in order to improve the biodegradation of recalcitrant compounds and minimize the sludge production. Many of the refractory or recalcitrant compounds are carcinogenic, mutagenic and detrimental to the environment. As toxicity standards have turn out to be more stringent, the development of new techniques for minimizing the concentration of bio refractory compounds and their breakdown products in the wastewater has become necessary. Protection of human health and the environment is now perceived as more important than the profitability and efficiency of a business.

The speciality chemical process requires large volumes of high purity water and generates equally large volumes of wastewater. These effluents are complex and characterized by high levels of chemical oxygen demand (COD), dissolved and suspended solids, a medium to low level of biochemical oxygen demand (BOD), a considerable amount of total organic halogen and an intense colour. Hence, the need for chemical treatment is necessary in order to produce a more readily biodegradable compound. Treatment technologies, which are discussed in the literature, include ozonation and coagulation [1], continuous treatment of textile wastewater by combined coagulation, electrochemical oxidation and activated sludge [2], wastewater treatment using chemical oxidation and physical adsorption [3], ozone treatment for bio-refractory COD removal [4], electrochemical treatment of wastewater containing organic pollutants [5], textile wastewater for reuse by means of different membrane processes [6], use of sequencing batch reactors and Fenton's reagent to treat a wastewater from a textile industry [7].

Application of conventional biological processes in the treatment of organic industry wastewater reported extensively in the literature which includes biotechnological transformations in effluent treatment [8], microbiological decolourization of an industrial effluent [9,10], hydrolytic dehalogenation of 4-chlorobenzoic acid by acinetobacter [11], combining photo-Fenton process with aerobic sequencing batch reactor for commercial hetero-bireactive dye removal [12], biodegradation of aromatic compounds [13–15], COD reduction and decolourization of textile effluent using combined process [16] and activated sludge treatment of dispersed

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dye factory wastewater [17]. The inability of biological treatment processes in degrading refractory compounds makes chemical treatment a necessary stage prior to bio treatment in order to produce more readily biodegradable materials by integration of chemical and biological oxidation processes for implementation [18]. The objective of this research is to evaluate the kinetics of a new combined electrochemical degradation and biological oxidation treatment system for an organic process industry. A thorough study of the optimum range of application for each method is a rather difficult task, but future work should be driven in this direction.

A first attempt [19] led to the choice of the technology in which wet air oxidation appears to be the most suitable technology for wastewater containing between 20 and 200 g L^{-1} of COD. The suitability of wet air oxidation would be further reinforced if a heterogeneous catalyst were successfully incorporated in the process. Wastewater with relatively small COD contents ($\leq$5 g L^{-1}) can be suitably treated by means of advanced oxidation processes since higher COD contents would require the consumption of too large amounts of expensive reactants. In these cases, it would be more convenient to use wet oxidation or incineration; wastewater with COD higher than 20 g L^{-1} may undergo autothermic-wet oxidation [20]. However the application of electrocatalytic oxidation makes the non-biocompatible organic effluent to biocompatible organic compounds. To make the effluent amenable for biological degradation it is preferred initially to adopt electrochemical treatment. If the biological degradation stops due to decay of endogenous cells, then electrochemical treatment is carried out once again and subsequently biological oxidation is continued. This sequence is to be repeated till the desired result is obtained. One of the main advantages of the electrochemical processes is that electrons are released or consumed within the electrodes, supplying a clean reactant, which does not increase the number of chemical molecules involved in the process.

Actual wastewater was used in this research was collected from a chemical industry, Sanmar Speciality Chemicals Limited, located at Berigai, near Hosur in Tamil Nadu; this unit manufactures performance chemicals for flavours and fragrances, resins, polymers and elastomers and intermediates for complex phytochemicals extracted from plants such as aloe vera, sunflower, etc. Typically this industry generates effluent around 35,000 L per day containing industrial solvents such as benzene, ethylbenzene, toluene, xylene and hexane and salt (sodium chloride was used for cleaning the equipments and the processing units). Before treatment the effluent contains COD 40,000–60,000 mg L^{-1}, SS 6000 mg L^{-1}, TDS 150 g L^{-1}, pH 7.3 and the colour is dark brown. In the present study, various experiments were conducted to reduce pollution load and reuse the water. The effluent typically contains COD about 48,000 mg L^{-1}. When it was distilled, the COD of the condensate reduces to 17,000 mg L^{-1} which was subjected to electrolytic degradation and subsequently biological oxidation was continued using various microorganisms such as *Bacillus subtilis, Pseudomonas aeruginosa* and *Proteus vulgaris* in a batch reactor.

If the output treated water is found unsuitable for processing in the industry, once again sent for treating to repeat the sequence till the desired result is obtained. This scheme constitutes an electrochemical–biochemical sequential reaction system.

2. Theoretical approach

2.1. Electrochemical degradation

The advantages of using electrochemical techniques (electrooxidation and electro-coagulation) include: environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation, and cost effectiveness [21]. The use of electrochemical technology has been widely studied as a method for the removal of organic substances [21–23]. Good removal rates were observed and it was suggested that the electrochemical method can be used as a pre-treatment step in pesticide waste disposal [24].

The dimensionally stable anodes (DSAs) are promising materials for many electro-organic applications and have been classified as 'active' or 'non-active', depending on its chemical nature [25,26]. Active electrodes mediate the oxidation of organic species via the formation of higher oxidation states oxides of the metal (MO_{x+1}), whenever a higher oxidation state can be reached by the metal oxide (e.g., RuO_2 or IrO_2)—leading to selective oxidation that makes the non-biocompatible organic effluent to biocompatible organic compounds. Non-active electrodes present no higher oxidation state available and the organic species is directly oxidized by an adsorbed hydroxyl radical, generally resulting in complete combustion of the organic molecule (e.g., SnO_2 or PbO_2). Titanium substrate insoluble anodes (TSIA) with RuO_X–IrO_X–TiO_X coating [27] anodes were employed in the present investigation since these electrodes are commercially available and are well known anode material for use in neutral chloride media.

2.1.1. Electro-coagulation (EC)

This is a process involving many chemical and physical phenomena in which the coagulating ions are produced in situ and it involves three successive stages: formation of coagulants by electrolytic oxidation of the sacrificial electrode, destabilization of the contaminants, particulate suspension (and breaking of emulsions) and aggregation of the destabilized phases to form flocs.

Electro-coagulation has been successfully employed in industrial effluents for removal of organic contaminants, oil and greases. In this process, a potential is applied to the metal anodes, typically fabricated from either iron or aluminum, which causes two separate reactions. Iron upon oxidation in an electrolytic system produces iron hydroxide, Fe $(OH)_n$, where n = 2 or 3. Mechanisms [28–30] that were proposed for the production of $Fe(OH)_n$ are:

Anode:

$$Fe \rightarrow Fe^{3+} + 3e^- \quad E^\circ = -0.04\,V \tag{1}$$

$$Fe \rightarrow Fe^{2+} + 2e^- \quad E^\circ = -0.04\,V \tag{2}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad E^\circ = -0.77\,V \tag{3}$$

$$4Fe^{2+} + 2H_2O + O_2 \rightarrow 4Fe^{3+} + 4OH^- \quad pH > 7 \tag{4}$$

$$4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 4H_2O \quad pH < 7 \tag{5}$$

Cathode:

$$2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O \quad pH > 7 \tag{6}$$

$$2H_3O + 2e^- \rightarrow 4OH^- \quad pH < 7 \tag{7}$$

The $Fe(OH)_n$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation [31]. In the surface complexation mode, the pollutant acts as a ligand (L) to chemically bind hydrous iron:

$$L\text{-}H(aq)(OH)OFe(s) \rightarrow L{\cdot}OFe(s) + H_2O(1) \tag{8}$$

The prehydrolysis of Fe^{3+}cations also leads to the formation of reactive clusters for treatment. The performance of electro-

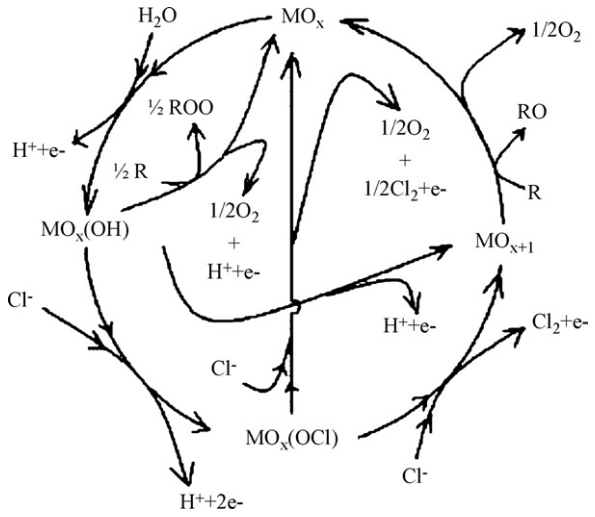

Fig. 1. Scheme of the electrochemical conversion/combustion of organics on noble oxide coated catalytic anode.

coagulation is well-described by the pseudo first-order kinetics.

$$-\frac{dL}{dt} = kL \quad \text{or} \quad -\frac{d[COD]}{dt} = k[COD] = k_L a[COD] \tag{9a}$$

Or

$$[COD] = [COD]_o \exp(-k_L a t) \tag{9b}$$

2.1.2. Electro-oxidation (EO)

The mechanism of electrochemical oxidation of wastewater is a complex phenomenon involving coupling of electron transfer reaction with a dissociate chemisorptions step. Basically two different processes occur at the anode; on anode having high electro-catalytic activity, oxidation occurs at the electrode surface (direct electrolysis); on metal oxide electrode, oxidation occurs via surface mediator on the anodic surface, where they are generated continuously (indirect electrolysis). In direct electrolysis, the rate of oxidation is depending on electrode activity, pollutants diffusion rate and current density. A generalized scheme of the electrochemical conversion/combustion of organics on noble oxide coated catalytic anode (MO_x) is shown in Fig. 1. In the first step, H_2O is discharged at the anode to produce adsorbed hydroxyl radicals according to the reaction.

$$MO_x + H_2O \rightarrow MO_x(^\bullet OH) + H^+ + e^- \tag{10}$$

In the second step, generally the adsorbed hydroxyl radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hydroxyl radical to the oxide forming the higher oxide MO_{x+1}.

$$MO_x(^\bullet OH) \rightarrow MO_{x+1} + H^+ + e^- \tag{11}$$

At the anode surface the active oxygen can be present in two states. Either as physisorbed (adsorbed hydroxyl radicals ($^\bullet$OH) or/and as chemisorbed (oxygen in the lattice, MO_{x+1}). In the absence of oxidizable organics, the active oxygen produces dioxygen according to the following reactions:

$$MO_x(^\bullet OH) \rightarrow MO_x + \tfrac{1}{2}O_2 + H^+ + e^- \tag{12}$$

$$MO_{x+1} \rightarrow MO_x + \tfrac{1}{2}O_2 \tag{13}$$

When NaCl is used as supporting electrolyte, Cl ion may anodically react with $MO_x(^\bullet OH)$ to form adsorbed OCl radicals according to the following:

$$MO_x(^\bullet OH) + Cl^- \rightarrow MO_x(^\bullet OCl) + H^+ + 2e^- \tag{14}$$

Further, in presence of Cl ion, the adsorbed hypochlorite radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hypochlorite radical to the oxide forming the higher oxide MO_{x+1} according to the following reaction and also $MO_x(^\bullet OCl)$ simultaneously react with chloride ion to generate active oxygen (dioxygen) and chlorine according to the following reactions:

$$MO_x(^\bullet OCl) + Cl^- \rightarrow MO_{x+1} + Cl_2 + e^- \tag{15}$$

$$MO_x(^\bullet OCl) + Cl^- \rightarrow MO_x + \tfrac{1}{2}O_2 + Cl_2 + e^- \tag{16}$$

In the presence of oxidizable organics, the physisorbed active oxygen ($^\bullet$OH) could cause predominantly the complete combustion of organics and chemisorbed will participate in the formation of selective oxidation [25,26] products according to the following reactions:

$$\tfrac{1}{2}R + MO_x(^\bullet OH) \rightarrow \tfrac{1}{2}ROO + H^+ + e^- + MO_x \tag{17}$$

$$R + MO_{x+1} \rightarrow RO + MO_x \tag{18}$$

The physisorbed route of oxidation is the preferable way for waste treatment. Since the organic hydrogen peroxides formed are relatively unstable, decomposition of such intermediates leads to molecular breakdown and formation of subsequent intermediates with lower carbon numbers. These sequential reactions continue until the formation of carbon dioxide and water [32,33]. In this case the diffusion rate of organics on the anode area controls the combustion rate [5,34]. On the other hand, temperature, pH and diffusion rate of generated oxidants determine the rate of oxidation in indirect electrolysis. In the same way indirect electrochemical oxidation mechanism has been proposed for metal oxide with chloride as supporting electrolyte for wastewater treatment [35–37]. In indirect electro-oxidation, chloride salts of sodium are added to the wastewater for better conductivity and generation of hypochlorite ions. The reactions of anodic oxidation of chloride ions to form chlorine in bulk of solution is given as

$$Cl_2 + H_2O \xrightarrow{k_1} H^+ + Cl^- + HOCl \tag{19}$$

$$HOCl \underset{k_{2'}}{\overset{k_2}{\leftrightarrow}} H^+ + OCl^- \tag{20}$$

$$\text{Organic} + OCl^- \xrightarrow{k_4} CO_2 + H_2O + Cl^- + P \tag{21}$$

Since organic compounds of the effluent are electrochemically inactive, the primary reaction occurs at the anodes is chloride ion oxidation (Eqs. (15) and (16)) with the liberation of Cl_2, which is a robust oxidizing agent. As regards to the reactions in the bulk, gaseous Cl_2 dissolves in the aqueous solutions due to ionization as indicated in Eq. (19). The rate reaction is less in acidic solution due to OH^- instability and considerably more in basic solution due to ready formation of OCl^- (pK_a 7.44) ion in Eq. (20) implying that the basic or neutral pH conditions are more favorable for conducting reactions involving chlorine. The direct electro-oxidation rate of organic pollutants depends on the catalytic activity of the anode, on the diffusion rate of the organic compounds in the active points of anode and applied current density. The indirect electro-oxidation rate of organic pollutants depends on the diffusion rate of the oxidants into the solution, flow rate of the effluent, temperature and the pH. In moderate alkaline solution a cycle of chloride–chlorine–hypochlorite–chloride takes place, which produces OCl^-. The pseudo steady state theory can be applied to each of the intermediates products (HOCl and OCl^-) taking part in the bulk solution. Taking all other reactions are irreversible processes, the rates of reactions r_i for the sequence are

$$-r_{Cl_2} = k_2[Cl_2] \tag{22}$$

$$r_{HOCl} = k_2[Cl_2] - k_3[HOCl] + k'_3[H^+][OCl^-] = 0 \quad (23)$$

$$rOCl^- = k_3[HOCl] - k'_3[H^+][OCl^-] - k_4[organic][OCl^-] = 0 \quad (24)$$

$$-r_{organic} = k_4[organic][OCl^-] \quad (25)$$

Then using the above equations we can easily deduce the following expression:

$$-r_{Cl_2} = -r_{organic} = k_4[organic][OCl^-] \quad (26)$$

Finally as regard to bulk solution it is also to be noted that $-r_{Cl_2} = -r_{Cl^-}$ from material balance of Eq. (19), that is

$$-r_{Cl_2} = r_{Cl^-} = k_2[Cl_2] = -r_{organic} = k_4[organic][OCl^-] \quad (27)$$

where the rate of reaction r_i and the rate constants k_i (i = 2, 3 and 4) are defined with respect to bulk and the rate expression for main electrode reaction as per Eq. (1) can be written as.

$$-r'Cl^- = r'Cl_2 = k_1[Cl^-]. \quad (28)$$

where k_1 is heterogeneous electrochemical rate constant. Hence, in the following section an attempt has been made to establish a relation between the reacting species in bulk and at the electrode surfaces. The basic relationship applicable to all electrochemical reactions is Faraday's law that relates to the amount of substance reacted at the surface to the charge ($I_A t$) passed is $M_A I_A t/nF$ (assuming 100% current efficiency) and the characteristic measurable parameter is current density, i_A, which is I_A/A_e. Thus the electrochemical reaction rate (for the disappearance of reactant A) can be expressed as

$$-\frac{(V_R/A_e)d[A]}{dt} = \frac{i_A}{nF} \quad (29)$$

where I_A is the current passed in time t, M_A is the molecular weight, n is the number of electrons transferred per mole of reaction, A_e electrode area, V_R reactor volume and F is the Faraday (96,500 C or As/mol). It has to be noted $-r_A = -d[A]/dt = i_A a/nF$ where a is specific electrode area (A_e/V_R). Assuming the main electrode reaction is governed by a simple Tafel type expression, then

$$-\frac{(V_R/A_e)d[A]}{dt} = \frac{i_A}{z_F} = k'[A]\exp(bE) \quad (30)$$

or

$$-r'_{Cl} = r'_{Cl_2} = k_1[Cl^-] = k'_1 a[Cl^-]_s \exp(bE) \quad (31)$$

The reaction may be assumed to be under diffusion control as the reacting species, Cl^- in the electrolyte is dilute. The reactant Cl^- is transported for the bulk to electrode surface where it under goes electrochemical oxidation to Cl_2 and it may be transported back to bulk by diffusion reaction in the bulk. Then,

$$\frac{i_A}{zF} = k_L([Cl^-] - [Cl^-]_s) \quad (32)$$

Elimination of $[Cl^-]_s$ using Eqs. (16) and (17) results as

$$\frac{i_A}{zF} = k_1[Cl^-] \quad (33)$$

where

$$\frac{1}{k_1} = \frac{1}{k_L} + \frac{1}{k'a\exp(bE)} \quad (34)$$

From a material balance of species Cl^- by taking note of Eqs. (12) and (13) we can write

$$\frac{i_A}{zF} = k'[Cl_2] \quad (35)$$

$$\frac{i_A}{zF} = k''[organic][OCl^-] \quad (36)$$

During electrolysis, since the constant current is applied, the rate of generation of $[OCl^-]$ will remain constant under a given set of experimental condition, but it varies as the applied current is altered. Then

$$\frac{i_A}{zF} = k_{obs}[organic] = k[COD] \quad (37)$$

Adopting the same classification for the reactors as for conventional reactors, thus the electrochemical reaction rate (for removal of COD) can be expressed as

$$-\frac{(V_R/A_e)d[COD]}{dt} = \frac{i_A}{zF} = k[COD] \quad (38)$$

In electrochemical conversion the high molecular weight aromatic compounds and aliphatic chains are broken to intermediate products for further processing.

2.2. Kinetics of biochemical oxidation

Understanding of the biochemical activities of the important microorganisms is the basic information to design a biological treatment process. In order the microorganisms to reproduce and function properly, organisms must have a source of energy, carbon for synthesis of new cellular material, inorganic elements or nutrients. Organic nutrients (growth factor) may also be required for cell synthesis. Carbon and energy source usually referred to as substrate. Two of the most common sources of cell carbon for microorganisms are organic matter and carbon dioxide. The principal inorganic nutrients needed by microorganisms are nitrogen (N), sulphur (S), potassium (P), magnesium (Mg), calcium (Ca), etc. In addition to these inorganic nutrients needed, some organisms may also need organic nutrients.

Effective environmental control in biological waste treatment is based on the basic principle governing the growth of microorganisms. Bacteria can reproduce either by binary fission or by a sexual mode or by budding. Generally, they reproduce by binary fission (i.e. by dividing, the original cell becomes two new organisms). The time required for each division is termed, the generation time, can vary from days to less than 20 min. For bacteria would not continue to divide indefinitely because of various environmental limitations, such as substrate concentration, nutrient concentration, or even system size. Different growth rate can be used for bacterial growth like, growth in term of bacterial numbers, growth in term of bacterial mass and growth in term of mixed cultures.

To ensure that the microorganisms will grow, they must be allowed to remain in the system long enough to reproduce. This period depends on their growth rate, which is related directly to the rate at which they metabolize or utilize the waste. Assuming that the environmental conditions are controlled properly, controlling the growth rate of the microorganisms can ensure effective waste stabilization. In both batch and continuous culture systems the rate of growth of bacterial cells can be defined by the following relationship

$$r_g = \frac{dX}{dt} = \mu X \quad (39)$$

where r_g = rate of bacterial growth, μ = specific growth rate, X = concentration of microorganisms. Because $dX/dt = r_g$ is for batch culture and is also valid for batch reactor. In batch culture, if one of the essential requirements either substrate or nutrients for growth were present only in limited amounts, it would be depleted first and growth would cease, in continuous culture, growth is limited. Experimentally it has been found that the effect of a limiting substrate or nutrient can often be defined adequately using the

following expression proposed by Monod.

$$\mu = \mu_m \frac{S}{k_s + S} \tag{40}$$

where μ = maximum specific growth rate, S = concentration of growth-limiting substrate in solution, k_s = half-velocity constant, substrate concentration at one-half the maximum growth rate. If the value of μ is substituted in Eq. (39), the resulting expression for the rate growth rate is

$$\frac{dX}{dt} = \mu_m \frac{XS}{k_s + S} \tag{41}$$

In both batch and continuous-growth culture systems, a portion of substrate are converted to new cell and a portion is oxidized to inorganic and organic end products. Because the quantity of the new cell produced has been observed to be reproducible for given substrate, the following relationship has been developed the rate of substrate utilization and the rate of growth.

$$\frac{dX}{dt} = -Y \frac{dS}{dt} \tag{42}$$

where Y = maximum yield coefficient (defined as the ratio of the mass of cell formed to the mass of substrate consumed). $r_{su} = dS/dt$ = Substrate utilization rate.

If the value of r_g from Eq. (41) substituted in Eq. (42), the rate of substrate utilization can be defined as follow:

$$\frac{dS}{dt} = -\mu_m \frac{XS}{Y(k_s + S)} \tag{43}$$

In Eq. (43), the term $\mu_m X/Y$is often replaced by the term C, defined as the maximum rate of substrate utilization.

If the term C is substituted in Eq. (43), the resulting expression is

$$\frac{dS}{dt} = -\frac{CS}{k_s + S} \tag{44}$$

In bacteria systems used for wastewater treatment, the distribution of cell age is such that not all the cells in the system are in the log-growth phase. Consequently, the expression for the rate of growth must be corrected to account for the energy required for cell maintenance. However, if most of the cells in the bacterial system are in lag-growth phase, the solution of Eq. (44) is

$$k_s \ln\left(\frac{S}{S_o}\right) + (S - S_o) = -Ct \tag{45}$$

where S_o is the initial substrate concentration. We can rewrite the Eq. (45) as

$$\frac{\ln(S/S_o)}{(S - S_o)} = -\frac{C}{k_s}\frac{t}{(S - S_o)} - \frac{1}{k_s} \tag{46a}$$

Or

$$-\frac{\ln(1 - x)}{x} = \frac{C}{k_s}\frac{t}{x} - \frac{S_o}{k_s} \tag{46b}$$

where x, the extent of substrate degradation is defined as $(S_o - S)/S_o$.

The plot of $\ln(S/S_o)/(S - S_o)$ vs. $t/(S - S_o)$ or $\ln(1 - x)/x$ vs. t/x will be linear if the above Monod's kinetics is followed. From the intercept half-velocity constant can be computed and the maximum utilization rate of substrate is obtained from slope.

The decrease in cell mass caused is proportional to the concentration of organisms present. This decrease is often identified in the literature as the endogenous decay. The endogenous decay term can be formulated as follows:

$$r_d(\text{endogenous decay}) = -k_d X \tag{47}$$

where k_d = endogenous decay coefficient.

When Eq. (47) is combined with Eqs. (39) and (41), the following expression are obtained for the net rate of growth

$$r'_g = \frac{\mu_m XS}{k_s + S} - k_d X \tag{48}$$

where r'_g = net rate of bacterial growth.

The corresponding expression for the net specific growth rate is given by

$$\mu' = \mu_m \frac{S}{k_s + S} - k_d \tag{49}$$

where μ' is the net specific growth rate.

The effect (of endogenous respiration on the net bacterial yield) are accounted for by defining an observed yield as follow

$$Y = \frac{r'_g}{r_{su}} \tag{50}$$

With the help of Eq. (48) and Eq. (50) we can expression for r'_{su}:

$$r'_{su} = \mu_m \frac{XS}{Y(k_s + S)} - \frac{k_d X}{Y} \tag{51}$$

If the value of r'_g from Eq. (51) is substituted in Eq. (42), the net rate of substrate utilization can be defined as follow:

$$\frac{dS}{dt} = -\mu_m \frac{XS}{Y(k_s + S)} + \frac{k_d X}{Y} \tag{52}$$

In this case the solution of Eq. (52) can be written as

$$\frac{\ln(S - A/B)/(S_o - A/B)}{(S - S_o)} = -\frac{B}{(k_s + A/B)}\frac{t}{(S - S_o)} - \frac{1}{k_s + A/B} \tag{53}$$

$$-\frac{\ln(1 - px)}{x} = \frac{B}{(k_s + A/B)}\frac{t}{x} - \frac{S_o}{k_s + A/B} \tag{54}$$

where

$$x = \frac{S_o - S}{S_O}; \quad \frac{A}{B} = \frac{k_d k_s}{\mu_m - k_d}; \quad B = \frac{\mu_m X}{Y} - \frac{k_d X}{Y}; \quad p = \frac{S_o}{S_o - A/B}$$

Benzene, toluene, ethylbenzene, and xylenes, collectively known as BTEX, are widely used as industrial solvents for extraction of intermediates and complex phytochemicals from plants such as aloe vera, sunflower, etc. and equipment cleansing. Since all BTEX compounds showed inhibition to cell growth, the Haldane's equation can be used in modeling the kinetics with high substrate concentrations which is often defined adequately using the following expression:

$$\mu = \mu_m \frac{S}{k_s + S + S^2/k_i} \tag{55}$$

where μ_{max} = maximum specific growth rate, S = concentration of substrate in solution, k_s = substrate affinity constant and k_i is substrate inhibition constant. The higher k_i value the less sensitive of the culture to substrate inhibition. The value of μ is substituted in Eq. (39). Consequently, the expression for the rate of growth must be corrected to account for the energy required for cell maintenance. However, if most of the cells in the bacterial system are in after lag-growth phase, the solution of equation is

$$k_s \ln\left(\frac{S}{S_o}\right) + (S - S_o) + \frac{S^2 - S_o^2}{2k_i} = -Ct \tag{56}$$

where S_o is the initial substrate concentration. We can rewrite Eq. (56) as

$$\frac{k_s \ln(S/S_o)}{(S - S_o)} + \frac{S}{2k_i} = -\frac{Ct}{(S - S_o)} - \frac{S_o}{2k_i} - 1 \tag{57}$$

If k_s is low then

$$\frac{S_o(1 - x)}{2k_i} = \frac{Ct}{S_o x} - \frac{S_o}{2k_i} - 1 \tag{58}$$

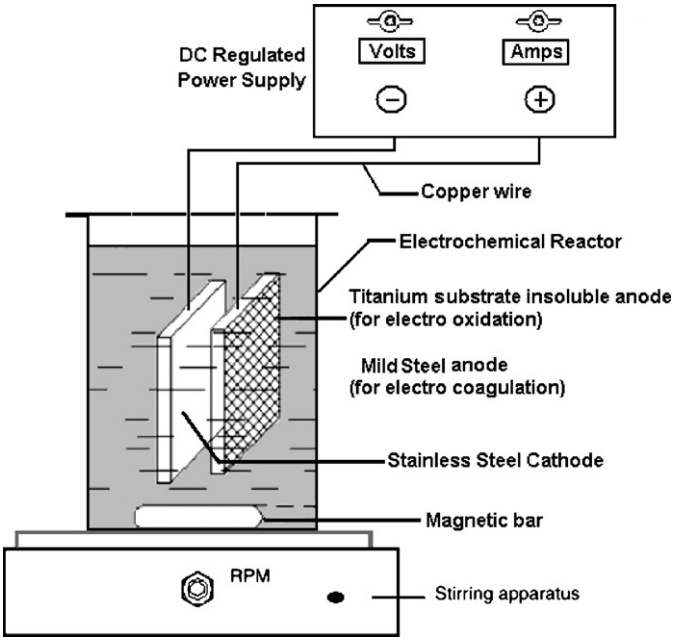

Fig. 2. Batch cell setup for electro-degradation.

where x, the extent of substrate degradation is defined as $(S_o - S)/S_o$. Simplifying the above expression as

$$x = -\frac{2k_i Ct}{S_o^2 x} + 2\left(1 + \frac{k_i}{S_o}\right) \quad (59)$$

3. Materials and methods

Actual effluents sample after a screening of solids was used in this research. The effluent was characterized before and after the combined electrochemical degradation and biological oxidation treatment, mainly in terms of chemical oxygen demand.

The chemical oxygen demand, total suspended solids (TSS), volatile suspended solids (VSS), oil and grease and pH were measured according to the American Public Health Association/standard methods for the examination of water and wastewater methods.

3.1. Electrolytic system

3.1.1. Electrochemical oxidation

A batch electrolytic cell (Fig. 2) was used for the electrochemical degradation process. The experimental setup consists of an undivided electrolytic cell of 240 mL working capacity, closed with a PVC lid having provisions to fix a cathode and an anode keeping 1.5 cm inter-electrode distance. A salt bridge with reference electrode was inserted through the holes provided in the lid. Titanium substrate insoluble anodes with a RuO_X–IrO_X–TiO_X coating (Subbiah et al. [27]) was an expanded mesh (of area 38 cm^2) was employed and a stainless steel plate (of dimension 6.0 cm × 4.0 cm × 0.2 cm) was used as the cathode. A multi-output 2 A and 30 V (DC regulated) power source (with ammeter and voltmeter) was connected to the cell. Stirring was done with a magnetic stirrer. The electrolyte taken was the distillated effluent (obtained after distillation of raw effluent).

3.1.2. Electro-coagulation

The experimental setup (Fig. 2) consists of an undivided electrolytic cell of 500 mL capacity (with working capacity of 240 mL) closed with a PVC lid having provisions to fix a cathode and a sacrificial anode. A salt bridge with reference electrode was inserted through the holes in the lid. The cathode was a stainless steel plate and anode was a mild steel plate both of size 6.0 cm × 4.0 cm × 0.2 cm kept in the cell maintaining inter-electrode distance of 1.5 cm. A DC regulated multi-output (2 A and 30 V) power source (with ammeter and voltmeter) was connected to the cell. Stirring was done with a magnetic stirrer. The electrolytes taken were the actual raw effluent and the distillated effluent (obtained after distillation of raw effluent) for investigation.

3.2. Microbial system

3.2.1. Microorganism and media

B. subtilis, P. aeruginosa, P. vulgaris strains were obtained from Microbiology Laboratory, Bharathidasan University, Trichy. A nutrient broth (100 mL distilled water containing peptone 0.5 g, yeast extract 0.3 g, sodium chloride 0.5 g was being sterilized at 121 °C, 1.1 kg m^{-2} for 20 min) has been prepared. The slant culture of various bacterial strains such as *B. subtilis, P. aeruginosa, P. vulgaris* were inoculated in the nutrient broth separately and then it was being kept in the incubator for its further growth. Initially microorganisms were grown aerobically at 37 °C and pH value 7 and further sub-culturing was done.

The nutrient medium containing grown microbes were serially diluted and made spread plate in agar plate and appeared colonies were counted after 24 h.

To eliminate the microbial adaptation period in the biodegradation experiments, microbes were pre-adapted to 100 mL medium and 5 mL of distillated effluent (where initially there was no degradation of effluent on the adaptation).

The cultures were acclimatized to effluent by exposing the cultures in a series of shake flasks wherein the content of peptone was decreased and that of effluent increased over a period of three months.

The temperature in all the batch experiments was maintained at 30 °C. The growths of the organisms were identified after 24 h by the turbidity nature by measuring optical density and the culture was maintained and all the inoculums transfers were done in exponential phase.

3.3. Electrolytic degradation

3.3.1. Procedure for electrochemical oxidation

The effluent of 240 mL was taken in a reactor. The required current was passed for predetermined interval of time using regulated power supply. During the electrolysis the cell voltage, electrode potentials were measured. A sample of 1 mL were collected at every 1 h and subjected to the COD analysis. Experiments were carried out for the distillated effluent. The experiments were carried out in this batch setup at the current density of 1 A dm^{-2} and which was conducted for different time intervals such as 1–7 h. That is for various charge input, the effluent was subjected to biological oxidation. Various experimental conditions, parameters measured and calculated are presented in the tables and figures.

3.3.2. Procedure for electro-coagulation

The effluent of 240 mL was taken in the cell. The required current was passed using regulated power supply. During the experiment the cell voltage, electrode potentials were measured. A sample of 1 mL was collected at every 1 h and subjected to the COD analysis. Experiments were carried out for the distillated effluent as well as raw effluent. The each experiment was carried out in a batch setup at different current densities viz 0.2, 0.4, 0.6 and 0.8 A dm^{-2}

and it was run for 7 h. The various experimental conditions and parameters measured and calculated are presented in the tables and figures.

3.4. Biological oxidation

3.4.1. Batch biochemical process

For biological treatment, after every additional hour of electrolytic degradation the effluent was taken out and subjected to biological oxidation. That is electrochemically partially degraded (treated) effluent been used as the (raw) effluent for biological oxidation. The experiment was carried out in a batch setup of 500 mL capacity beaker (with working capacity of 300 mL) was used. Effluents were collected at different time intervals of ranging from 1 to 7 h of electrochemical treatment to follow sequentially biochemical process.

The bacterial organisms such as *B. subtilis, P. aeruginosa* and *P. vulgaris* were tested against this industrial effluent. 100 mL of medium containing the culture such as *B. subtilis* was added to the 200 mL of the electrochemically treated wastewater. The total volume of 300 mL capacity of batch setup was being aerated with an aqua pump aerator for a period of 120 h. The samples were being collected every 24 h and it was subjected to COD analysis. The experiments were repeated for other cultures such as *P. aeruginosa* and *P. vulgaris*. The observations of various parameters were presented in tables and figures.

3.5. Error analysis

The least sum of the squares (SS) of the differences between the experimental data and the data obtained by calculating from the models SS could be computed. If data from the model are similar to the experimental data, SS will be a small number; if they are different, SS will be a large number. In order to substantiate the best fit model for the system, it is needed to analyze the data using the values of SS, combined with the values of the determined regression coefficient (R^2).

4. Results and discussion

4.1. Electrolytic system

4.1.1. Electrochemical oxidation and electro-coagulation

The experimental results of the electrochemical oxidation (EO) as well as of electro-coagulation processes are presented in Fig. 3a and Table 1 for the distillated effluent. In respect of electrooxidation process in the batch reactor, at 1 A dm^{-2} it was observed that the COD was decreased from 17,000 mg L^{-1} to 3600 (79% of COD removal) in 7 h for the applied current of 0.24 A (with charge input of 3.5 Ah L^{-1}) and with the average cell voltage of 8.3 V, the specific energy consumption on average of 5.9 kWh kg^{-1} of COD removal was obtained where as only 6% of COD removal was obtained after input of 0.5 Ah L^{-1}.

The results of the electro-coagulation experiments for various current densities were also shown in Fig. 3a and b for both the distillated as well as for the raw effluent. The effects of current density on transfer coefficient are shown in corresponding figure. In case of distillated sample, the system performance is more or less similar at operating current density of 0.8 A dm^{-2} (see Fig. 3) except that the specific energy consumption on average of 2.69 kWh kg^{-1} of COD removal was obtained. But for the raw effluent the % removal of COD in 7 h was around 59.0 at the highest current density.

The purposes of presenting above experimental results are only to have an idea before venturing the integration of electro- and biodegradation of above effluent. The effluent was distilled in a solar evaporator so as to reuse the reuse the distillate in processing.

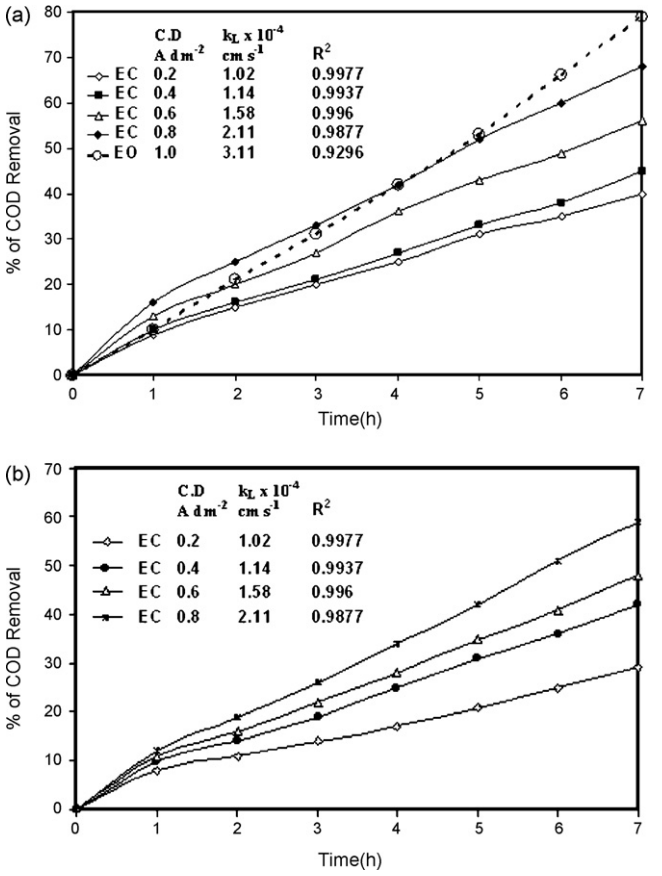

Fig. 3. (a) Extent of % removal of COD by degradation (EO and EC) for distillated effluent. (b) Extent of % removal of COD by degradation (EC) for raw effluent.

4.2. Microbial system

4.2.1. Batch biochemical process

The details of result of electrolytic oxidation and biological degradation of the effluent were presented in Fig. 3a, Fig. 4a–c as well in Table 1. That is the bacterial organism such as *B. subtilis, P. aeruginosa* and *P. vulgaris* were tested against the industrial effluent.

The results of the experiment was carried out in a batch setup after different charge input at 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 Ah L^{-1} (by electrochemical treatment) to continue sequentially biochemical process (by aeration with an aqua pump aerator) up to 120 h are presented in Fig. 4a for *B. subtilis*, Fig. 4b for *P. aeruginosa* and Fig. 4c for *P. vulgaris*.

Fig. 4a and Table 1 present the result of degradation by *B. subtilis* by electrochemical and biochemical in which the figures clearly indicate that there is remarkable change in the course of the degradation process. The % removal rate COD by biochemical in first day (in first 24 h) is kinetically different from next four days. At lower charge input (0.5 Ah L^{-1}) the removal rate is higher and decreases as charge per litre increases and at higher charge input (3.5 Ah L^{-1}) the removal rate is much lower on first day of biochemical oxidation but in the next four days the trends was marginally same. The % removal rate of COD by biochemical oxidation using *B. subtilis* is around 88% and the overall COD decreased was 97%.

Fig. 4b and Table 1 show the result of degradation by *P. aeruginosa* by electrochemical and biochemical in which the figures also indicate that there is remarkable change in the course of the degra-

Table 1
Effect of charge per liter on electrochemical–microbial sequential process in batch reactors in terms of COD removal by *Bacillus subtilis*, *Pseudomonas aeruginosa* and *Proteus vulgaris*.

Charge input Ah L^{-1}	Electrochemical		COD with Broth and Culture mg L^{-1}	*Bacillus subtilis*			*Pseudomonas aeruginosa*			*Proteus vulgaris*		
	COD after EO mg L^{-1}	% Removal of COD		COD after bio oxidation mg L^{-1}	% Removal of COD	Overall	COD after bio oxidation mg L^{-1}	% Removal of COD	Overall	COD after bio oxidation mg L^{-1}	% Removal of COD	Overall
0.5	16,000	5.88	12,000	2100	82.5	87.65	3376	71.87	80.14	2700	77.5	84.11
1	13,700	19.41	10,200	1955	80.83	88.5	1787	82.48	89.49	2382	76.64	85.99
1.5	11,800	30.58	8,800	1491	83.05	91.23	1492	83.05	91.22	1865	78.81	89.03
2	9,900	41.76	7,400	934	87.37	94.51	748	89.89	95.6	1496	79.79	91.2
2.5	8,100	52.35	6,100	753	87.65	95.57	678	88.88	96.01	1205	80.24	92.91
3	5,900	65.29	4,400	559	87.28	96.71	490	88.86	97.12	858	80.5	94.95
3.5	3,600	78.82	2,700	450	83.33	97.35	338	87.5	98.01	375	86.11	97.79

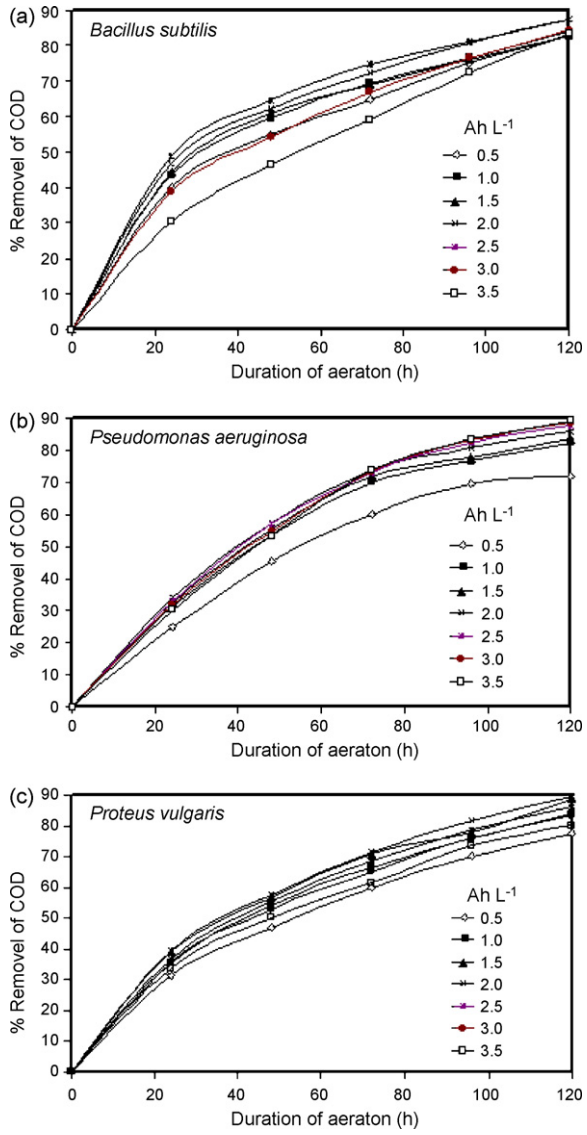

Fig. 4. Effect of charge input on % removal of COD of electrochemical–microbial sequential process on aeration in a batch reactor by (a) *Bacillus subtilis*, (b) *Pseudomonas aeruginosa* and (c) *Proteus vulgaris*.

dation process. The % removal rate COD by biochemical in first day (in first 24 h) is kinetically different from next four days. The performance is much better at lower charge inputs (0.5–2 Ah L^{-1}), the removal rate is higher than at higher charge inputs (2.5–3.5 Ah L^{-1}) the removal rate is lower on first day of biochemical oxidation but in the next four days more or less the trend maintains. The % removal rate of COD by biochemical oxidation using *P. aeruginosa* is around 86% and the overall COD decreased was 98%.

Fig. 4c and Table 1 show the result of degradation by *P. vulgaris* by electrochemical and biochemical in which the graphs clearly indicate that there is remarkable change in the course of the degradation process. The % removal rate COD by biochemical in first day (in first 24 h) is kinetically different from next four days. The performance is more or less same as above. The % removal rate of COD by biochemical oxidation using *P. vulgaris* is around 88% and the overall COD decreased was 98%.

Kinetics analysis of the data is important to develop an equation which accurately represents the results and which could be used for design purposes. Several kinetics equations have been used for

Table 2
Performance of electrochemical–microbial sequential process in batch reactors by *Bacillus subtilis, Pseudomonas aeruginosa* and *Proteus vulgaris*.

Charge	Exponential		Monod kinetics			Haldane's inhibition model			Monod kinetics with decay			
Ah L^{-1}	C/k_s h^{-1}	R^2	C mg L^{-1} h^{-1}	k_s mg L^{-1}	R^2	C mg L^{-1} h^{-1}	k_i mg L^{-1}	R^2	k_s h^{-1}	B mg L^{-1} h^{-1}	A/B	R^2
Bacillus subtilis												
0.5	0.01479	0.98961	98	13364	0.93575	35	11849	0.99181	13252	116	349	0.93125
1	0.01579	0.98117	88	11037	0.97288	31	9884	0.96424	10921	104	297	0.98117
1.5	0.01561	0.97297	71	9294	0.98351	26	8461	0.94821	9144	84	256	0.97999
2	0.01771	0.98642	80	8223	0.96298	24	7130	0.95871	8267	97	215	0.95226
2.5	0.01822	0.98048	66	6601	0.98233	20	5806	0.93441	6612	80	177	0.97395
3	0.01548	0.99488	41	5090	0.90942	13	4387	0.99798	5100	49	128	0.90321
3.5	0.01393	0.98581	22	3232	0.73695	7	2781	0.95419	3246	26	79	0.73301
Pseudomonas aeruginosa												
0.5	0.01162	0.97942	65	13299	0.90231	27	12237	0.89674	13075	152	1830	0.849
1	0.01518	0.99241	94	12013	0.84905	30	10340	0.94609	12165	127	485	0.87304
1.5	0.01574	0.98877	86	10322	0.85249	27	8868	0.94255	10482	116	419	0.88482
2	0.01703	0.99295	85	8945	0.82726	24	7449	0.94918	9107	104	215	0.8838
2.5	0.01772	0.99866	80	7776	0.78446	21	6206	0.9445	7807	99	177	0.88128
3	0.01816	0.99762	62	5799	0.75867	15	4512	0.92707	6320	87	128	0.78728
3.5	0.02068	0.91901	39	3620	0.74579	9	2783	0.90118	3848	51	78	0.74345
Proteus vulgaris												
0.5	0.01262	0.99761	79	13627	0.87861	30	12202	0.98782	13430	102	571	0.8839
1	0.01514	0.99752	94	11991	0.89535	30	10279	0.9932	11849	113	486	0.89194
1.5	0.01732	0.98604	106	10819	0.85188	29	8813	0.99378	11155	134	256	0.83101
2	0.01833	0.99459	103	9459	0.85928	26	7433	0.99688	9944	133	216	0.83877
2.5	0.01642	0.99815	67	7406	0.88125	20	6145	0.99411	7541	82	178	0.87403
3	0.01501	0.99701	40	5168	0.88501	13	4436	0.99702	5185	48	128	0.88125
3.5	0.01368	0.99595	20	3102	0.87958	7	2733	0.99168	3087	22	53	0.88097

the modeling of biochemical system. The most widely used is two parameters Monod kinetics model. In addition, exponential decay, Monod kinetics with endogenous decay and Haldane's inhibition to cell growth equation were also used for analysis. The model relates the variation of substrate concentration with time. For each model, for a given initial substrate concentration, the following three microbes: *B. subtilis (Bs), P. aeruginosa (Pa)* and *P. vulgaris (Pv)* were used microbial degradation. The kinetic model is characterized by certain constants, explicitly by maximum rate of substrate utilization, C, substrate affinity constant, k_s, endogenous decay coefficient, k_d and substrate inhibition constant, k_i which expresses COD removal with time. Exponential decay model, Monod kinetics, Monod kinetics with endogenous decay and Haldane's inhibition to cell growth equation constants are evaluated from the % of COD removal with time for three different microbes (*Bs, Pa* and *Pv*) and their regression coefficients are also presented in Table 2. High regression coefficients (mostly greater than 0.9) were found for all the microbes studied, suggesting that all models are very suitable for describing the kinetic model in that studied concentration. The applicability of all the models to the effluent implies that both substrate affinity and substrate inhibition exist under the experimental conditions used. This is due to the presence of biodegradable and refractory organic present in effluent. The degradation of effluent by microbes is thus complex, involving more than one mechanism. From Table 2, the Exponential decay model and Haldane's inhibition to cell growth equation is suited well for degradation of effluent by *P. vulgaris* compared to *Bs* and *Pa* as indicated by the high magnitude of regression coefficient (greater than 0.99), whereas the degradation pattern of effluent by *B. subtilis* found to obeys Monod kinetics model as well as Monod kinetics model with endogenous decay (which is evident from its high magnitude the regression coefficient).

The sequence of performance of microbes on biological degradation of effluent after the charging 0.5 Ah L^{-1} is *B. subtilis*, *P. vulgaris* and *P. aeruginosa* where as after charge input of 3.5 Ah L^{-1}, first day *P. vulgaris* dominates and in the next four days the performance of the sequence is *P. aeruginosa, P. vulgaris* and *B. subtilis*.

It is to be noted that the kinetic model that are characterized by constants, such as maximum rate of substrate utilization, substrate affinity constant, k_s, endogenous decay coefficient, k_d and substrate inhibition constant, k_i decreases as charge input increases for all microbes.

5. Conclusions

In the present study, it can be concluded that the refractory pollution load can be reduced to 2000 mg L^{-1} of COD at optimum condition experiments (around 2 Ah L^{-1} of charge input) with the distillated effluent containing 17,000 mg L^{-1} of COD when the effluent was subjected to electrolytic degradation and subsequently biological oxidation using any of the microbes such as *B. subtilis*, *P. aeruginosa* and *P. vulgaris* in a batch reactor. This output once again can be considered for treating electrochemically for removal of COD up to the prescribed limit so as to constitute an electrochemical–biochemical sequential reactor system.

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