

TROUBLE SHOOTING ISSUES OF BIODEGRADATION OF ORGANIC POLLUTANTS IN TROPICAL MARINE ENVIRONMENT

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Abstract

Marine pollution occurs due to the entry of organized or unorganized, point or non – point land based releases of industrial, agricultural and residential waste. Biodegradable organic waste rich in microorganisms lead to potentially harmful effects and alter oxygen cycle, where as excessive inputs of nutrients like nitrogen and phosphorus stimulate algal growth leading to eutrophication.

Thermodynamics play an important role in chemicals reactions occurring in ocean during degradation of organic waste. The rate of reactions is altered due to temperature and high salinities. This aspect is very crucial while predicting the self purification capacity of the water body. Adequate experimental work pertaining to the order of reaction and thermodynamic constants is essential to prove the basis of the predicted assimilative capacity of the system.

In Mumbai, huge quantity of domestic waste is generated. Due to land restrictions, complete treatment of tertiary level is not feasible. The Municipal administrators take the advantage of coastal location and discharge this waste into the ocean with just meagre preliminary treatment. The disposal practices are advanced and well planned but still expected purification or dilution is not achieved in the near shore region. This has resulted in spoiling the impact zone of coastal areas creating stress on the living biota and non compliance of the marine water quality standards.

Three major issues in coastal system, viz. Operation and control of waste discharges, degradation patterns of pollutants and self purification capacity needs systematic evaluation to maintain favorable conditions for aquatic life. Hence it is essential to study the reaction kinetics and thermodynamic behaviour of the biodegradation of carbonaceous waste occurring under highly saline conditions. Experiments are conducted to confirm the kinetics and thermodynamics of biodegradation of domestic waste water into marine water at variable salinities. The paper presents the findings of kinetic behaviour particularly the values for rate of reaction, Activation energy and related constants.

Key words: BOD, kinetics of biodegradation, thermodynamic aspects of BOD

INTRODUCTION

Background

Water, a finite natural resource and the best solvent for the chemical reactions, is essential to sustain life & conserve environment. Chemical composition of water is essentially defined by parameters, viz. pH, dissolved oxygen (DO), biochemical oxygen demand (BOD) and nutrients like nitrogen, phosphorus etc. Inorganic, organic & hazardous wastes released into the water bodies contaminate the system. Fate of organic pollutants released in water body, is decided by the fundamental kinetic formulations which are based on DO & BOD. Decay of carbonaceous organic matter is a complex “Redox” reaction, also termed as “Wet oxidation”. Dissolved Oxygen is an essential parameter for aquatic life, an oxidizer and cleansing agent. Marine coastal region faces ecological stress due to indiscriminate waste discharges and DO sag curve is distorted due to pollution.

Hypothesis for Self Purifications Reactions in Coastal Water¹ states that “The rate of breakdown of organic compounds through biodegradation, decomposition and ratification actions in marine water is slow, temperature dependent and has varied reaction rate constant”. Hence it is essential to study the kinetics of reaction expected during degradation process. Reaction Kinetics (or Chemical Kinetics) is the quantitative study of chemical reactions and is rate of reaction is affected by different parameters like reactant concentration, temperature, ionic strength and catalyst etc. Temperature has the most profound effect on reaction rate.

Concept of Chemical Kinetics, Activated Complex and Thermodynamic formulae:

Chemical kinetics provides information about the reaction mechanism responsible for the conversion of complex pollutants (reactants) into simpler harmless stable products. The biodegradability, expressed in terms of Biochemical Oxygen Demand (BOD) is one of the most common tests for the determination of the breakdown of organic content of wastewater. The decay of biodegradable carbonaceous organic matter follows first order kinetics². The BOD decay rate determined in a laboratory might not necessarily be the same as estimated for a natural water body. The kinetic parameters “k” (rate constant) is mainly governed by the salinity and temperature in marine waters. While deciding the quality and quantity of waste releases, rate constant (k) for biodegradation under varying salinities needs critical consideration to ultimately achieve receiving water quality standards.

Law for first order chemical kinetics applied to carbonaceous BOD states that the rate of decomposition is directly proportional to the amount of undecayed material and is mathematically expressed as $\{-dC/dt = kC\}$. The – ve sign indicates loss of material with time, C the concentration and “k” the rate constant for the reaction. It has units of reciprocal of time.

Reaction rates are related to the activated complex theory and are interpreted in terms of a transient short lived species called activated complex formed during the course of the reaction. In all chemical reactions, an intermediate activated complex is formed when the reactant molecules possessing the energy of activation E come together and undergo effective collisions to form the activated complex which then results in products. The rearrangement of the atoms and bonds of the reactant molecule form the activated complex. The activated complex is a transient species and breaks up into products³. This threshold energy for the reaction is related to other thermodynamic activation parameters like enthalpy of activation, free energy of activation and entropy of activation. These parameters indicate the spontaneous/non-spontaneous nature of the reaction. The energy of activation is additional energy, which the reactant molecules must acquire in order to form the activated complex.

Reactants (A) + (B) $\rightarrow$ Activated complex [X] $\rightarrow$ Products.

Rate constant $k = k_B T K^*/h$ where h is the Plank's constant

In such chemical reaction, the equilibrium constant K^* is related to the rate constant of the reaction "k" by the relation

$$K = k_B T K^*/n$$

where K_B is the Boltzman constant $1.38 \times 10^{-23} \text{ JK}^{-1}$

Further the enthalpy of activation ΔH^* is related to energy of activation E by the equation

$$\Delta H^* = E + \Delta nRT$$

where Δn is the change in the number of molecules when the activated complex X is formed from the reactant molecules.

For the carbonaceous oxygen demand reaction expressed as "Organic matter C + O₂ $\rightarrow$ X $\rightarrow$ CO₂ + biomass", $\Delta n = 1-2 = -1$, Hence above equation reduces to

$$\Delta H^* = E - RT$$

The free energy of activation ΔG^* is related to the equilibrium constant K^* by the relation

$$-\Delta G^* = 2.303 RT \log K^*$$

The entropy of activation ΔS^* is related ΔH^* and ΔG by the relation

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

$$\text{Hence } \Delta S^* = \Delta H^* - \Delta G^*/T$$

For a spontaneous reaction, ΔG is negative and ΔS is positive and for a non-spontaneous reaction, ΔG is positive and ΔS is negative. From the effect of temperature on reaction rate, the thermodynamic activation parameters like E , K^* , ΔH^* , ΔG^* and ΔS^* were calculated for the biochemical reaction "organic matter C + O₂ = CO₂ + biomass".

Calculations of temperature dependence of Reaction rate and thermodynamic activation parameters

The effect of temperature on reaction rate is most profound. Arrhenius equation quantifies the effect of the temperature on the reaction rate

$$k = A.e^{-E/RT}$$

where A is the frequency factor and E is the energy of activation of the reaction which represents the energy that reactant molecules must acquire in order to take part in the reaction. The above equation can be modified to the form where k_1 and k_2 are the rate constants at absolute temperatures T_1 and T_2 respectively.

The energy of activation of the reaction (E) was calculated using a modified formula of Arrhenius equation viz.

$$\log \frac{k_2}{k_1} = \frac{E}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

where k_1 and k_2 are the rate constants in s⁻¹ at absolute temperature T_1 and T_2 respectively.

MATERIALS AND METHODS

BOD test measures oxygen requirement for aerobic stabilization of the organic matter. Since it is a bio-assay test, identical test conditions were maintained to get reliable data. The natural sea water with 35-36 ppt of salinity has about 20,000 mg/L of chlorides. The chloride concentrations were varied to represent creek, estuaries and ocean conditions. The dilution media were buffered to provide adequate nutrients. The artificial seawater as described by B.Loganthan⁴ was used. The experiments were conducted for 10 days to achieve the maximum exertion of carbonaceous BOD. Experimental details are presented in Table 1.

Table 1: Details of experimental set up for BOD estimation

Sl. No.	Selected Parameter	Description of Values	
1	Temperature	20°C and 27°C	
2	dilution media	Buffered distilled water with 0, 5000, 10000, 15000 and 20000 mg L ⁻¹ Chlorides	
3	Duration & Frequency	10 Days with every day BOD estimation	
4	Test Samples	Synthetic	Environmental
5		Glucose – Glutamic Acid (GGA) solution	Domestic waste water (Sewage)
6	Biodegradability	Good	Good

Due to limited solubility of oxygen in salty water and based on the expected BOD, necessary dilution was done. A settled raw sewage was used as seed to provide heterogeneous population of microorganisms. The BOD tests were carried out as per standard Methods⁵. A glucose glutamic acid solution of 250 mg/L each was used. The domestic wastewater from wastewater treatment facility of Mumbai represents environmental sample. The 90% theoretical BOD² as determined from chemical formula of glucose glutamic acid and a COD value for domestic wastewater were considered as “ultimate BOD”.

The samples incubated for various time slots were also analyzed for the existence and adequacy of heterotrophic microorganisms using Zobel/Nutrient agar media. All the experiments were carried out in triplicate and the average values considered for calculations. To evaluate BOD exertion pattern and kinetics, theoretical BOD from the chemical formula of Glucose – glutamic acid and COD value of domestic wastewater was considered as ultimate BOD. It is proved that the BOD at 20°C for 5 days is equivalent to the BOD at 27°C for 3 days⁶. Hence both temperatures were selected for incubation. “k” was estimated through computer based software. Statistical Parameters like correlation coefficient & linear regression were evaluated to assess goodness of fit of values using equation {y = mx + c}. Thermodynamic activation parameters were calculated using modified Arrhenius equation.

RESULTS AND OBSERVATIONS

The analytical results and the subsequent analysis for thermodynamic parameters along with the reaction constant “k” values are presented below:

Table 2: BOD exertion of Glucose–Glutamic acid with varying chloride Concentrations

Glucose Glutamic acid solution with ultimate BOD (L) as 480 mg/L					
Days	% Exertion of Average BOD at 20°C				
	0 mg/L chlorides	5000 mg/L chlorides	10000 mg/L chlorides	15000 mg/L chlorides	20000 mg/L chlorides
1	22.3	27.3	14.8	9.1	8.5
2	38.1	46.9	32.9	13.3	14.8
3	44.4	50.2	46.9	34.2	32.9
4	64.0	55.2	51.0	40.4	37.7
5	70.2	59.0	53.1	41.7	46.0
Days	% Exertion of Average BOD at 27°C				
	0 mg/L chlorides	5000 mg/L chlorides	10000 mg/L chlorides	15000 mg/L chlorides	20000 mg/L chlorides
1	48.5	49.0	33.7	8.7	6.9
2	57.7	53.0	54.6	44.8	45.0
3	69.4	58.5	58.7	51.9	50.0
4	77.1	71.7	66.4	51.9	54.1
5	87.5	74.6	72.1	62.9	58.3

Table 3: Percent BOD exertion of Sewage with varying chloride concentration in the dilution media

Sewage with ultimate BOD (L) as 300 mg/L					
Days	% Exertion of Average BOD at 20°C				
	0 mg/L chlorides	5000 mg/L chlorides	10000 mg/L chlorides	15000 mg/L chlorides	20000 mg/L chlorides
1	22.3	14.0	17.3	19.3	19.0
2	33.3	25.3	24.7	25.3	26.3
3	50.3	29.3	31.3	29.3	28.0
4	51.6	33.7	34.7	33.0	28.3
5	55.7	34.3	38.3	34.0	31.3
Days	% Exertion of Average BOD at 27°C				
	0 mg/L chlorides	5000 mg/L chlorides	10000 mg/L chlorides	15000 mg/L chlorides	20000 mg/L chlorides
1	32.3	23.3	23.3	22.3	26.0

2	39.7	32.0	31.0	33.3	34.0
3	56.0	42.3	42.0	34.7	36.7
4	62.7	45.3	45.3	37.0	40.7
5	66.7	47.7	48.0	41.3	42.3

Table 4: Values of rate constant “k” at 20°C and 27°C

Chloride content mg/L	A		D	
	20°C-5 day	27°C-3 day	20°C-5 day	27°C-3 day
0	0.24	0.46	0.20	0.28
5000	0.25	0.39	0.12	0.18
10000	0.18	0.33	0.13	0.18
15000	0.11	0.20	0.13	0.16
20000	0.11	0.19	0.13	0.18

A = Glucose Glutamic acid solution with ultimate BOD (L) as **480 mg/L**

D = sewage with ultimate BOD (L) as **300 mg/L**

Table 5: Thermodynamic Activation Parameters at 20°C and 27°C for the reaction “organic matter C + O₂ → CO₂ + biomass”.

Chloride mg L ⁻¹	Temp. K	K (day ⁻¹)	k (s ⁻¹)	E (kj)	K*x1 0 ¹⁹	ΔH* (kj)	ΔG* (kj)	ΔS*(kj) K ⁻¹ mol ⁻¹
(A) Glucose Glutamic Acid								
0	293 K	0.24	2.778 x10 ⁻⁶	67.86	4.55	65.42	102.90	-0.1279
0	300 K	0.46	5.324 x10 ⁻⁶		8.52	65.37	103.79	-0.1281
5000	293 K	0.25	2.894 x10 ⁻⁶	46.42	4.74	43.98	102.80	-0.2007
5000	300 K	0.39	4.514 x10 ⁻⁶		7.22	43.93	104.20	-0.2009
10000	293 K	0.18	2.083 x10 ⁻⁶	63.27	3.41	60.83	103.60	-0.1460
10000	300 K	0.33	3.819 x10 ⁻⁶		6.11	60.78	104.62	-0.1462
15000	293 K	0.11	1.273 x10 ⁻⁶	62.45	2.09	60.01	104.80	-0.1529
15000	300 K	0.20	2.315 x10 ⁻⁶		3.70	59.96	105.87	-0.1531
20000	293 K	0.11	1.273 x10 ⁻⁶	57.02	2.09	54.58	104.80	-0.1714
20000	300 K	0.19	2.199 x10 ⁻⁶		3.52	54.53	106.00	-0.1716
(D) Sewage								
0	293 K	0.20	2.315 x10 ⁻⁶	31.69	3.79	29.29	103.34	-0.3230
0	300 K	0.28	3.241 x10 ⁻⁶		5.19	29.20	105.03	-0.3231
5000	293 K	0.12	1.389 x10 ⁻⁶	38.20	2.28	35.76	104.59	-0.1778
5000	300 K	0.18	2.083 x10 ⁻⁶		3.33	35.71	106.14	-0.1775
10000	293 K	0.13	1.504 x10 ⁻⁶	30.69	2.46	28.25	104.39	-0.2529
10000	300 K	0.18	2.083 x10 ⁻⁶		3.33	28.20	106.14	-0.2528
15000	293 K	0.13	1.504 x10 ⁻⁶	19.57	2.46	17.13	104.39	-0.2349
15000	300 K	0.16	1.853 x10 ⁻⁶		2.96	17.08	104.39	-0.2348
20000	293 K	0.13	1.504 x10 ⁻⁶	30.69	2.46	28.25	106.14	-0.2599
20000	300 K	0.18	2.083 x10 ⁻⁶		3.33	28.20	104.39	-0.2598

OBSERVATIONS

The following are the observations recorded from the laboratory study:

- BOD decreased progressively with increase in chloride concentration thereby indicating the negative impact of chlorides on the oxidation of carbonaceous matter.
- BOD exertion was 10 to 15 % higher at 27°C as compared to 20°C for all media. This significant increase in oxidation of Glucose Glutamic acid and sewage at 27°C emphasizes important role of temperature and needs critical evaluation for tropical regions.
- The comparable values of BOD exerted at 20°C, 5days and 27°C, 3days proved the hypothesis of equivalence of BOD exertion at above temperature and duration. The observation permits to adopt the test period of shorter duration at elevated temperature for marine environment also.
- Adequate microorganisms were present at all chloride concentrations for the whole test period at both the temperatures. Existence, survival and multiplication of microbes were not the limiting factor for reducing trend in BOD exertion.

- The “k” values had lowered with increase in chloride concentrations. This finding confirmed the slowing down of the rate of biodegradation of organic matter with elevation of chlorides (salinity). Hence more time will be required to break down the pollutants and this aspect needs to be considered while planning waste discharges in the marine environment.
- Calculations of thermodynamic activation parameters for effect of Temperature on Reaction rate indicates that the lowering of free energy of activation due to increase in rate constant with temperature is more than compensated by the increase in ΔG^* due to increase in temperature. The net result is that at a given temperature, it is observed that higher the rate constant, lower is ΔG^* . The findings confirm the anticipation and can be stated as:

The rate constant k increases with the absolute temperature. The equilibrium constant K^* for the formation of activated complex also increases with temperature, hence K^* is also a function of temperature. An increase in the temperature is accompanied by a slight increase in free energy of activation ΔG^* .

There is a very slight decrease in the enthalpy of activation (ΔH^*) with increase in temperature. This may be due to solute – solvent interaction which may restrict the degrees of freedom of the solvent molecules. For a given system, an entropy of activation (ΔS^*) remains nearly constant at both temperatures. The negative value of ΔS^* indicate a decrease in the degree of freedom due to the formation of a rigid activated complex as a transient intermediate during the course of the reaction. The negative ΔS^* values may indicate an extensive reorientation of solvent molecules as a result of the formation of the activated complex¹ leading to a decrease in disorder (non – spontaneous reaction).

SUMMARY AND CONCLUSIONS

10 to 15 % higher BOD was observed at 27°C when compared to 20°C for all media. Negative impact of chlorides on the oxidation of organic matter was observed showing decrease in BOD exertion at higher chloride concentrations. The hypothesis of equivalence of BOD exertion at 20°C, 5day and 27°C, 3days was confirmed for selected salinities. This observation permits adoption of BOD test at 27°C with shorter duration for saline waters. Nitrogenous oxidation was not considered at selected test conditions till 5 days. However, additional oxygen will be required for nitrogenous BOD and needs consideration while designing waste discharges. Availability of microbes was not the limiting factor for reduction trend in oxidation of organic matter at increased chloride concentrations. Rate constant k increases with temperature in accordance with Arrhenius equation but decreases with increasing salinity. Equilibrium constant K^* for the formation of the activated complex from the reactant molecules, also increases with temperature but decreases with increasing salinity. Hence K^* is a function of temperature. Negative Entropy of activation and Positive Gibbs Free Energy of Activation values indicate that the reaction is non-spontaneous

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