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REVIEW ON ADVANCES IN BIODEGRADATION OF PHENOLS: KINETICS, MODELLING AND MASS TRANSFER

Ladi Reshma [1], V. Sridevi [2], M. N. N. Sai Rachana [1], J. Akhila [1], M. Yamini [1], Katru Ramya Sugandhi [1], Husam Talib Hamzah [3], R. Sri Harsha [1]

[1] M. Tech Biotechnology, Department of Chemical Engineering, AU College of Engineering (A), Andhra University, Visakhapatnam, India
[2] Professor, Department of Chemical Engineering, Andhra University, Vishakhapatnam-530003, India
[3] Ph.D. Scholar, Department of Chemical Engineering, Andhra University, Vishakhapatnam-530003, India

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CorrespondingAuthor

Ladi Reshma,
ladi.reshma123@gmail.com

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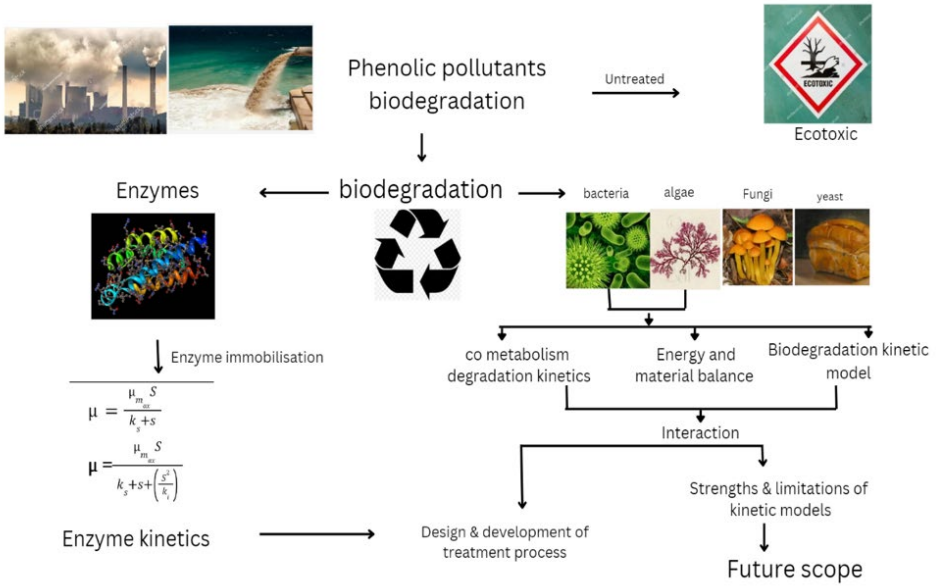
ABSTRACT

Harmful pollutants like phenol and its derivatives are found in wastewater from a wide range of industries, including oil refining, medicines, coal conversion, chemistry, and petrochemistry. The high concentration, high toxicity, and difficult-to-degrade characteristics of phenols in wastewater pose a serious threat to the environment and to human health. By employing different strains of microorganisms and biocatalysts to create biodegradation procedures of diverse pollutants and a wide spectrum of hazardous compounds, biotechnology has successfully addressed significant environmental challenges. Among various phenols removal techniques, biodegradation is both economical and environmentally friendly. During the study of microbial degradation processes, there is a great deal of interest in the potential for mathematical modelling to forecast microbial growth and degrade harmful or inhibiting environmental pollutants at variable quantities. Such mathematical models are frequently created using aromatic compounds like phenol. The review discusses the following topics: kinetics, modelling, and mass transfer; future scope and directions; diverse microorganisms, bioreactors, the metabolic pathway of phenol, influencing factors, and recent advancements in biological therapy.

Keywords: Biodegradation, Phenol, Mechanism, Immobilization, Modelling, Kinetics, Mass Transfer

HIGHLIGHTS

- The manufacturing of paper, coking, insecticides, plastics, and pharmaceuticals are only a few of the industrial processes that produce phenol, which has a very broad range of sources.
- An intricate process involving the creation of several enzymes is required to biodegrade the aromatic molecule phenol.
- When organic matter, in this case phenolic compounds, is transformed into carbon dioxide, this process is known as carbon mineralization.
- To explore the kinetics of phenol biodegradation in the SBR mode and to compare the findings with the available data, the Haldane equation (Eq. This formula is used to calculate the rate at which an inhibiting substrate degrades.



1. INTRODUCTION

As industrial production increased and the demand for chemicals increased, massive amounts of phenol-tainted effluent were discharged into waterways. Phenol and its derivatives were chosen due to their extensive industrial use and threat to aquatic life Duan et al. (2018). The removal of various dangerous organic compounds from wastewater can be accomplished using three main techniques: non-destructive, oxidative destructive, and biologically destructive. Since non-destructive methods rely on the physical adsorption and removal of contaminants, they produce a lot of waste. Oxidative destructive methods include incineration, moist oxidation, and complex oxidation processes (AOPs). Although oxidative destruction may be able to eliminate contaminants, the cost of the necessary equipment, operations, and maintenance make it difficult to use. Biological activities consume a lot less energy and chemicals than other types of processes.

One of the biggest challenges to microbial pollutant degradation is the inability to retain enough biomass for the biodegradation of a target molecule. Antimicrobials can be used to treat both inhibiting compounds like phenols and microbiological illnesses in living things. If either is present, it may cause a die-off of microorganisms in the bioreactor and ineffective wastewater treatment. Although maintaining the bioaugmented culture in a bioreactor can be difficult, adding certain bacterial cultures to a system (bioaugmentation) may expedite the breakdown of antimicrobial contaminants and resistant chemicals Kuc et al. (2022). The washout and dilution of the suspended bacterial culture in a bioreactor are frequently brought on by the continuous injection of wastewater to the reactor. To get around these difficulties in biological degradation, researchers have created a variety of methods for immobilising microbial cultures as well as methods for accelerating phenol degradation through the use of kinetics, modelling, and mass transfer.

2. ORGANIC POLLUTION OF PHENOL

Today's population must regularly deal with a frustrating issue that includes land pollution, water contamination, other environmental problems, and air pollution Sun et al. (2022). One of the most pressing environmental problems on a global scale is organic pollution, which has risen quickly in importance due to the

rapid development in urbanisation and industrialization Touliabah et al. (2022). Water that has been tainted with phenolic pollutants is challenging to clean up since they arrive in a variety of concentrations from various industrial processes. Phenolic compounds are present in wastewater and are dangerous to both people and the environment because of their high solubility in water and sluggish rate of biodegradation. for a variety of reasons. Even at modest doses, phenols and phenolic compounds are toxic to human health, and many of them are considered dangerous pollutants as a result, Aminophenols, butylhydroxytoluene, nonylphenols, and bisphenols are only a few examples of the phenolic substances Aisami et al. (2020).

1) SOURCE OF PHENOLS

Typically, the primary environmental sources of phenol are man-made or natural materials. It results from its processing and use in many contexts, such as, for example, wood burning and automotive exhaust Khleifat et al. (2007). Endogenous and exogenous phenolic compounds are the two types of phenolic compounds that are frequently found in nature Sun et al. (2022). Endogenous phenols are phenolic chemicals that are present in nature and have biological effects. They frequently include the leaves, stems, fruits, roots, and other plant or crop elements. The by products are exogenous phenols. Exogenous phenols and substituted phenols, mostly from vehicle exhaust and smoke from burning biomass, were present in the air. Related phenolic compounds are also created during the production and processing of industrial items. During the coking and refining processes, phenol was one of the principal ingredients obtained from coal and oil mines Wang et al. (2011), Viraj et al. (2017). The creation of oil and its by products, fibreglass, steel, furnace coke, cork, explosives, paint, the manufacture and recycling of rubber products, the textile industry, and several segments of the food and beverage industry are just a few industrial processes that produce phenols Bhatia et al. (2018).

2) LIMITS OF PHENOL

The EPA has established a threshold for phenol in surface water of fewer than 1 ppb Kazemi et al. (2014). The toxicity thresholds are typically between 9 and 25 mg/L for both aquatic life and humans. Phenol may have immediate or long-term negative consequences on one's health. Humans who are exposed to toxic compounds over an extended period of time may have deadly dosages of respiratory risks, tremor, weakness, and erratic breathing. The National Institute for Occupational Safety and Health (NIOSH REL), which stands for "NIOSH Recommended Exposure Limit," specifies the upper limit or exposure limit for an 8- or 10-hour timeweighted average. The acceptable exposure limit, or OSHA PEL, is the maximum concentration of a material to which most employees can be exposed without suffering adverse consequences. It is a time-weighted average across a normal 8-hour workday or 40-hour workweek. The United States Environmental Protection Agency (USEPA) recommends that lead levels in drinking water not go over 0.05 mg/l Kazemi et al. (2014).

3) HARMFUL EFFECTS OF PHENOL

In addition to cancer and genetofibre striation, severe phenol exposure produces disorders of the central nervous system, hepatic damage, anorexia, cutaneous rash, dysphasia, gastrointestinal disturbance, vomiting, weakness, and weightlessness González et al. (2001). According to an animal study, oral phenol

exposure results in decreased foetus weights, delayed growth, and aberrant development in the offspring of the animals. Increased maternal mortality and decreased maternal weight gain were also discovered González et al. (2001).

2.1. ANALYSIS OF PHENOL

Numerous techniques, including spectrophotometry, HPLC, GC, and their combinations, have been employed to measure phenolic chemicals from plant materials as analytical science has advanced.

2.1.1. SPECTROPHOTOMETRY

Spectrophotometry, which largely relies on many measurement techniques for the different structural changes of the phenolic compounds, is a rapid and simple methodology for figuring out how much phenolic compounds are present in plant materials. Typically, the content of flavonoids is determined using spectrophotometry. (2016) Pouraboli et al. Additionally, condensed tannin concentration and total phenolic amount can both be determined using spectrophotometry Sankhalkar and Vernekar (2016). Spectroscopy is a frequently utilised technique for quantifying many different types of phenolic compounds due to its simplicity of use and inexpensive cost.

2.1.2. GAS CHROMATOGRAPHY (GC)

GC is a useful method for separating, identifying, and measuring the numerous phenolic chemicals present in plants, including anthocyanins, flavonoids, and tannins. Samples are heated in a heated column that uses the evaporation temperature specific to each compound to separate it from the solution. The column is lined with a thin layer of non-volatile liquid that is coated with an inert substrate Vaičiulyte et al. (2016).

2.1.3. HIGH-PRESSURE LIQUID CHROMATOGRAPHY (HPLC)

The most popular method for separating and detecting phenolic chemicals is HPLC. It is a flexible and adaptable tool with a number of benefits, including good selectivity, sensitivity, resolution, and sample behaviour Naczk and Shahidi (2006). The basic idea behind the method is to separate chemicals from complex mixtures based on how soluble they are and/or how they interact with a less polar stationary phase and a more polar mobile phase Coskun (2016). Thus, some variables, including column types, used detectors, mobile phase, and the characteristics of the tested substances, have an impact on HPLC analysis of phenolic compounds.

2.1.4. HPLC–MASS SPECTROMETRY

HPLC and tandem MS can be used to examine phenolic substances. An innovative analytical method with great sensitivity and selectivity is HPLC supplemented by MS detection. With this method, unidentified chemicals in samples of natural sources that have been partially or crudely purified can have their structural information measured. Mocan et al. (2014). Numerous studies on the analysis of phenolic compounds have recently concentrated on the evaluation of techniques including various couplings between HPLC and MS.

2.1.5. HPLC–DIODE ARRAY DETECTOR

Another popular technique for determining the presence of phenolic compounds in plants is HPLC combined with a diode array detector (HPLC-DAD). Da Silva Siqueira et al. (2016), Alqahtani et al. (2015).The most expensive and uncommon of the detectors used in conjunction with HPLC to the identification of phenolic chemicals is MS, whereas the most practical and widespread is DAD Rejczak and Tuzimski (2017).The entire UV/visible spectrum of the analytes can be simultaneously scanned by the DAD detector, which can also provide details on unique spectral characteristics for compound identification.

3. METABOLIC PATHWAYS FOR PHENOL

An aromatic hydrocarbon called phenol is broken down by a variety of bacteria, which obtain all of their carbon needs from phenol. Both aerobic and anaerobic environments can lead to the degradation of phenol.

3.1. AEROBIC BIODEGRADATION OF PHENOL

Oxygenation starts the biodegradation of phenol under aerobic conditions. A monooxygenase phenol hydroxylase first monohydroxylates the aromatic ring in this process at an ortho location to the pre-existing hydroxyl group to produce catechol. This is the primary intermediate produced when various microbial strains break down phenol. Depending on the strain, catechol is either oxidised by catechol 1,2-dioxygenase via the ortho-cleavage pathway, which results in the creation of succinyl Co-A and acetyl Co-A, or by catechol 2,3-dioxygenase via the meta-pathway, which results in the formation of pyruvate and acetaldehyde Patil et al. (2014).

3.2. ANAEROBIC BIODEGRADATION OF PHENOL

The aerobic phase of phenol decomposition is more advanced than the anaerobic process. The aerobic phase of phenol decomposition is more advanced than the anaerobic process. The first step in the anaerobic process is the 4-hydroxy benzoate carboxylase-mediated carboxylation of phenol at the para position to 4-hydroxybenzoate. Carboxylation and subsequent dihydroxylation are the mechanisms through which phenolic chemicals, such as o-cresol, catechol, and ortho-halogenated phenol, are degraded by anaerobic bacteria González et al. (2001). Figure 1 and Figure 2 shows aerobic and anaerobic degradation pathway for phenol.

Figure 1

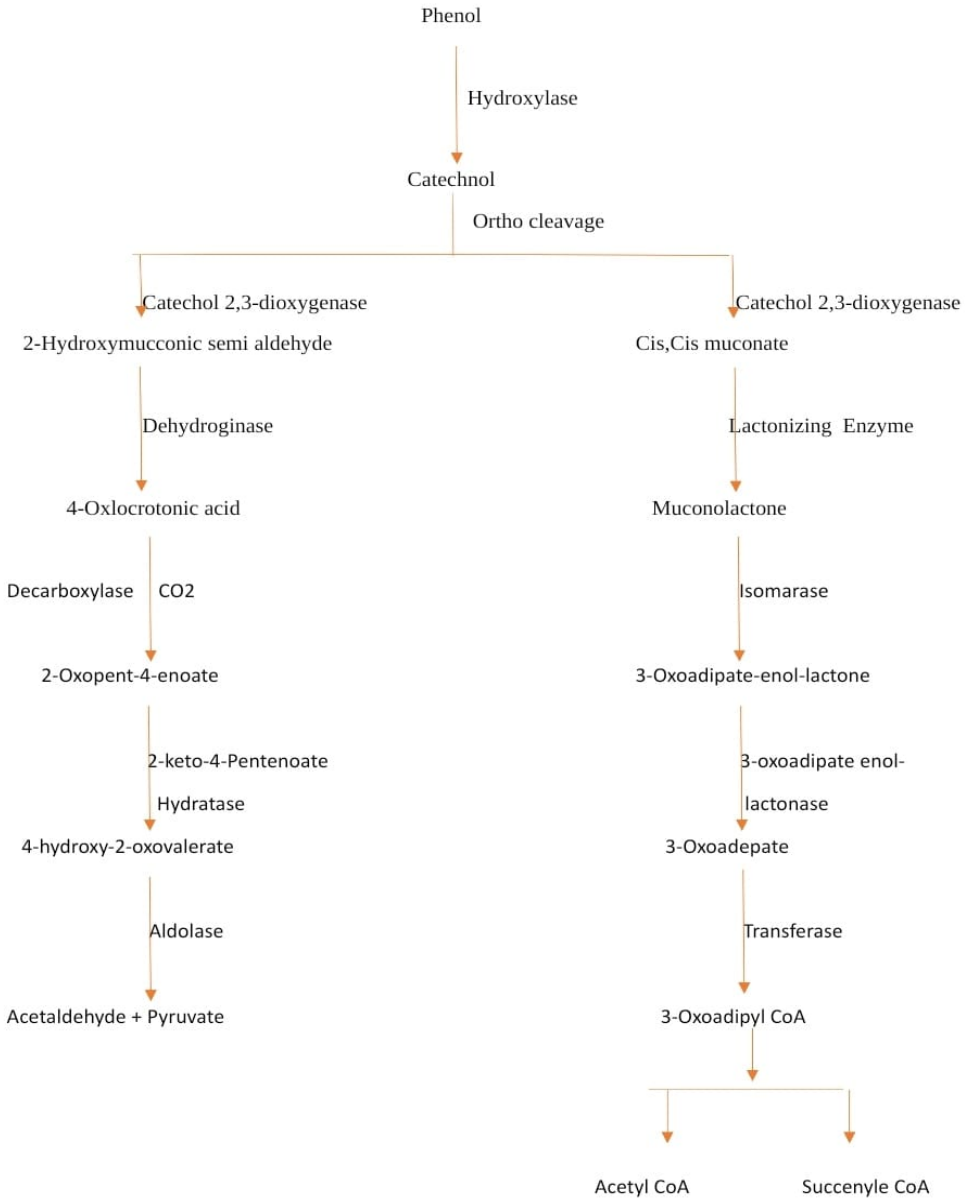


Figure 1 Aerobic Degradation Pathway for Phenol

Figure 2

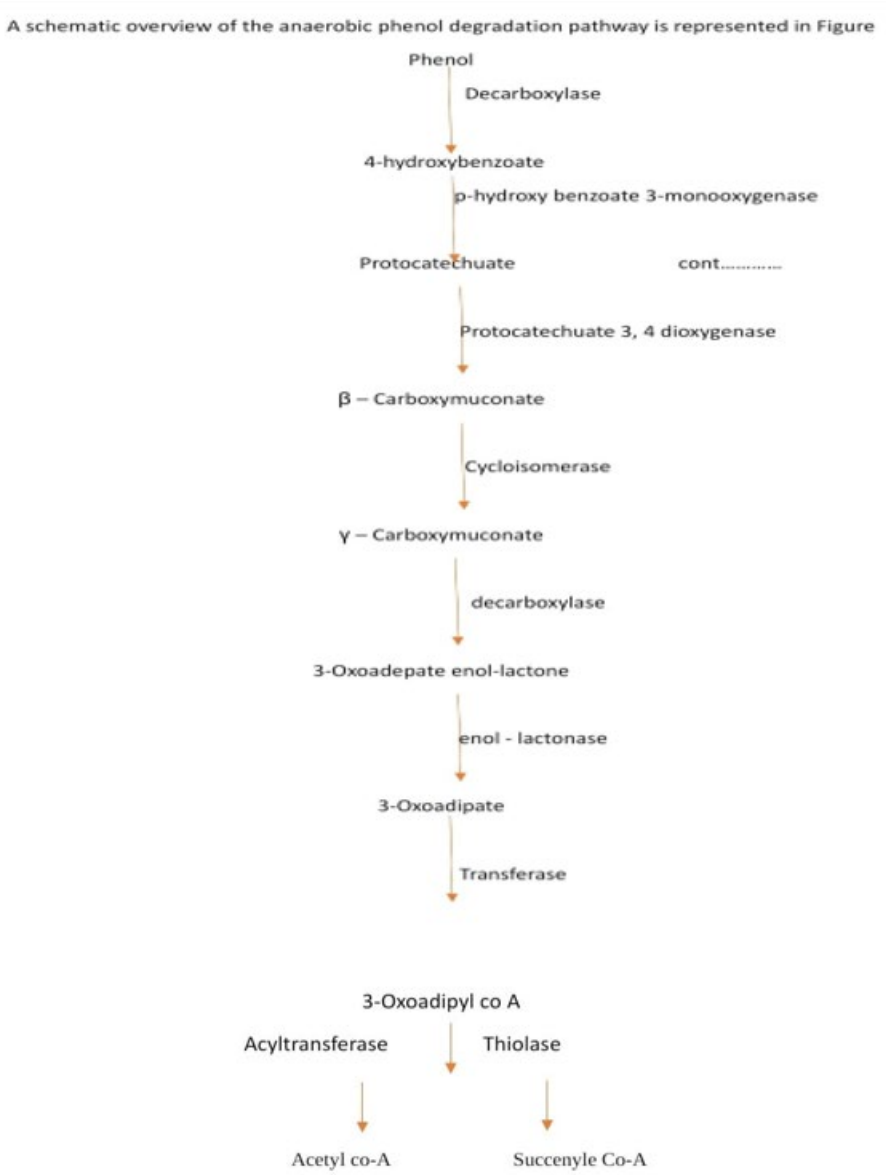


Figure 2 Anerobic Degradation Pathway for Phenol

4. MECHANISM, VARIOUS MICROORGANISMS, AND REACTORS FOR PHENOL BIODEGRADATION

Phenol, an aromatic hydrocarbon is degraded by various microorganisms, Table 1 which utilizes phenol as the sole carbon source for the growth of the organisms. Among the various microorganisms *Pseudomonas putida* is the most popular organism for the degradation of phenol as this species uses phenol as the carbon source . Numerous microorganisms—including both aerobic and anaerobic ones—use phenol as their only source of carbon and energy as a result of the substance's extensive prevalence in the environment. The presence of phenolic compounds in water and soil has become significant problems. Common commercial wastewater treatment methods utilize the combination of physico-chemical and biological treatment. Both chemical and biological processes were

used for many years to treat phenolic wastewater. Activated sludge, fluidized, packed bed and moving bed biofilm reactors were studied as biological treatment processes. Table 2 shows various reactors used in phenol degradation and their effect. The degradation rate depends on the state of biomass development, feed concentration, liquid flow rate, and air flow rate.

4.1. DEGRADATION OF PHENOL THROUGH AEROBIC AND ANAEROBIC PATHWAYS

4.1.1. AEROBIC BIODEGRADATION OF PHENOL

At the beginning of the 19th century, research on aerobic biodegradation began. The enzyme phenol hydroxylase uses molecular oxygen to add a second hydroxyl group in ortho-position to the one that already exists in the initial phase of the aerobic route for the biodegradation of phenol. Pyridine nucleotide reduction is necessary for the process (NADH2). Depending on the causative bacterium, one of two procedures can then be used to get rid of the resultant catechol (1, 2- dihydroxy benzene) molecule. A catechol 1, 2-dioxygenase splits the aromatic ring between the catechol hydroxyls via the ortho- or ketoadipate pathway (intraradiol fission) Harwood and Parales (1996). The first to provide circumstantial evidence that strain "Vibrio 01" generated -ketoadipate while metabolising phenol was Evans and Kilby Evans (1947).

The resultant cis, cis muconate undergoes further metabolism to create -ketoadipate, which is a Krebs cycle intermediate. Ring fission takes place in the meta-pathway close to the two hydroxyl groups of catechol (extra diol fission). Catechol 2, 3-dioxygenase is an enzyme that changes catechol into 2-hydroxymuconic semialdehyde. This chemical is converted into Krebs cycle intermediates by further metabolism. Acinetobacter calcoceticus, Pseudomonas species, and Candida tropicalis use the aerobic pathway to consume phenol, whereas other eukaryotes frequently use the ortho pathway. Numerous studies have focused on the aerobic Pseudomonas species, and their capacity to grow on a range of aromatic substrates makes them an appealing organism for use in wastewater treatment applications Kilby (1948).

4.1.2. ANAEROBIC BIODEGRADATION OF PHENOL

The first stage of the anaerobic phase of this process is the carboxylation of phenol at the para position to 4 hydroxybenzoate. The 4-hydroxybenezoate carboxylase is the enzyme in question here. It has been demonstrated that a carboxylation reaction is a key component of the anaerobic decomposition of many more aromatic compounds. It has been proposed that o-cresol can be denitrified to produce 3-methyl 4-hydroxybenzoate by carboxylating the aromatic ring in para position to the hydroxy group. Studies demonstrated that Para coccus-like organisms and the methogenic consortia moved through a variety of phenolic chemicals, including catechol, ortho halogenated phenols, and o-cresol, after para Dehydroxylation, followed by carboxylation.

Table 1

Table 1 Phenol Degrading Microorganisms Fan et al. (2008)

Source	Genus	Species
Bacteria	*Alcaligenes*	*Alcaligenes faecalis*
		Alcaligenes xylosoxidans Y234
		Arthobacter species
	Anthrobacter	*Arthobactercitreus*
		Arthobacterchlrophenolicus A6
		Pseudomonas putida
		Pseudomonas cepacian
		Pseudomonas pictorum
	Pseudomonas	*Pseudomonas aeruginosa MTCC 4996*
		Pseudomonas aeruginosa
		Pseudomonas aeruginosa CC7CCAB919095
		Cyanobacterium synechococcus
		Bacillus species strain PHN1
	Cyanobacterium Bacillus	*Bacillus brevis*
		Bacillus badius
Fungi	*Candida*	*Candida Tropicalis*
		Candida Tropicalis NICM 3556
	Fusarium	*Fusarium species*
	Graphium	*Graphiumsp FIB4*
	Ochromonas	*Ochromonasdanica*
	Aspergillus	*Aspergillus awamori NRRL3112*
Yeast	*Phanerochaete*	*Phanerochaetechrysosporium*
	Rhodococus	*Rhodococuserythropolis UPV-1*
	Rhodotorula	*Rhodotorulacreatinivora*
	Sphigmonas	*Sphigmonaschlorophenica R4 2*
	Trichosporon	*Trichosporon species LE3*
		TrichosporonCutaneum R57

Table 2

Table 2 Reactors Used in the Phenol Degradation Khazi Et Al. (2010)

S.No	Reactor	Organisms Used	Effect On Phenol Degradation
1	Packed bed Reactor	*Rhodococcus erythropolis*	Able to degrade completely phenol in defined mineral medium at a maximum rate of 18kg of phenol m-3 per day
2	Air stirred Reactor.	*Rhodococcus erythropolis* UPV-1	Completely degrade phenol in synthetic wastewater at a volumetric productivity of 11.5 kg of phenol/m3 /day

3	Packed bed Reactor	*Alcaligenes xylosoxidans* Y234	Able to degrade phenol of 1000 ppm completely in 60 h
4	Hallow Fiber Membrane bioreactor	*Pseudomonas putida*	Able to degrade phenol of 1000 – 2000 mg/L
5	Rotating biological contactors (RBC)	Mixed culture	Input loading 1754 – 3508 mg phenol/m2h
6	Air lift bioreactor	*Alcaligenes xylosoxidans* and *Xanthomonas maltophilia*	The fractional conversion of phenol over 99% was achieved
7	Loop airlift bioreactor with a packed bed.	*Pseudomonas putida ATCC 17484*	100% phenol removal was achieved at phenol loading rates up to 33120 mg /h m
8	Pulsed plate bioreactor	Immobilized *Nocardia hydrocarbonoxydans*	100% degradation could be achieved with 300 and 500ppm influent phenol concentrations and at very low dilution. rate of 0.4094 1/h
9	Self-cycling Fermentation in a stirred tank reactor	*Pseudomonas putida*	Substrate utilization rates as high as 14.5 kg of phenol per cubic meter of fermentor volume per day of Fermentation,
10	Granular activated carbon was incorporated into hollow fiber membrane bioreactor.	*Pseudomonas putida*	1000 ppm phenol was removed within 25 h.

5. EFFECTS OF PARAMETERS FOR BIODEGRADATION OF PHENOL

5.1. EFFECT OF PH

It is believed that the internal environments of all living cells are fairly neutral. A pH of 4.0 or above is inhospitable to the majority of life. At pH 4.0 or 9.0, acids and bases typically don't dissociate from one another and are resistant to electrostatic fields, making them easier to enter cells. The optimal pH for phenol breakdown in Pseudomonas putida NICM 2174 is 7.0. Annadurai et al. (2002).

5.2. EFFECT OF TEMPERATURE

The key factor in the breakdown of organic contaminants is temperature, not the presence of nutrients. Numerous investigations revealed that the rate of phenol biodegradation considerably decreased around 30 °C Pakuła et al. (1999). The majority of studies on phenol degradation have been done in the laboratory at the ideal temperature of 30°C, and they also found that as the temperature increased from 30 to 34°C, no phenol degradation happened due to cell death, demonstrating

that phenol decomposition is a temperature-dependent process Annadurai et al. (1999). Growth rates typically double for every 10°C increase in temperature in the typical mesophilic working range of 10 to 30°C.The denaturation of proteins at higher temperatures lowers mesophile growth rates, but growth rates in general do not vary between 35°C and 40°C Ratkowsky et al. (1982).

5.3. EFFECT OF ADDITIONAL CARBON SOURCES ON PHENOL DEGRADATION

Diverse strategies have been put out to handle highly concentrated phenolic wastewater by discovering ways to get around substrate inhibition. These include the use of genetically engineered microorganisms, cell immobilisation, and phenol concentration adaption. One may be able to boost the cells' tolerance to substrate inhibition by supplementing the growth medium with additional conventional carbon sources, like yeast extract or glucose. Yeast extract has also been seen to boost Pseudomonas putida's affinity for phenol Armenante et al. (1995).

5.4. EFFECT OF DISSOLVED OXYGEN CONCENTRATION

Most frequently, oxygen serves as the ultimate electron acceptor in aerobic respiration in aerobic microorganisms. Additionally, the microbial breakdown of a variety of organic molecules, including hydrocarbons and compounds with aromatic rings, requires a co-substratum known as molecular oxygen. The rate of organic load breakdown under aerobic growth conditions is mostly determined by the dissolved oxygen (DO) level. In studies on this subject, much attention has been paid to how dissolved oxygen content affects microbial growth and respiration rate.

6. ADVANCES IN BIODEGRADATION OF PHENOL: KINETICS, MODELING, AND MASS TRANSFER

6.1. KINETICS AND MODELLING

Studies on the kinetics of biodegradation reactions give an indication of how effectively the microbial system is working. Gaining an understanding of these dynamics will improve phenol removal efficiency and process control. By tying a certain biomass growth rate to a specific substrate consumption rate, any biodegradation process may be predicted (contaminant). A variety of kinetic models have been used to describe the kinetics of microbial growth on phenol Table 3.

Two of the most popular models for the biodegradation of phenol are the Monod model Table 3, Equation 1 and the Haldane (Andrew's) model Table 3, Equation 2.

Table 3

Table 3 Biodegradation Models (Kinetics and Mass Transfer) Taghreedalkhalid et al. (2012)

Name of model	Equation
Monad	$\mu = \frac{\mu_{max} S}{k_s + s}$ Equation 1
Haldane	$\mu = \frac{\mu_{max} S}{k_s + s + \left(\frac{s^2}{k_i}\right)}$ Equation 2
Linearized haldane	$\frac{1}{\mu} = \frac{1}{\mu m_{ax}} + \frac{s}{k_i \mu_{max}}$
Han- Levenspiel	$\mu = \frac{\mu_{max}\left[1 - \frac{s}{s_m}\right]^n}{K_s + s - \left[1 - \frac{s}{s_m}\right]^m}$
Yano	$\mu = \frac{\mu_{max} S}{s + k_s + \left(\frac{s^2}{k_i}\right)\left[1 + \frac{S}{k}\right]}$
Edwards	K is a constant $\mu = \mu_{max}\left[exp\left(\frac{-s}{k_i}\right) - exp\left(\frac{-s}{ks}\right)\right]$
Wang-Loh[2]	$-\frac{ds}{xdt} = \frac{RS}{k_s + s + f(i)}$ $f_{(i)} = \frac{(S_0 - S^2)}{k_P}$ $X = X_0 e^{\mu} t$ $\mu = \frac{\mu_{S_0}}{k_s + s_o + \left(\frac{s_o^2}{k_i}\right)}$
Monod: Sum Kinetics Binary mixture, no interaction	$\mu = \frac{\mu_{,1}\, s_1}{k_{s,1} + s_1} + \frac{\mu_{,2}\, S_2}{k_{s_{,2}} + s_2}$
Monod: sum kinetics Binary mixture, purely competitive interaction (inhibition)	$\mu = \frac{\mu_{,1}\, s_1}{k_{s,1} + s_1 + \left(\frac{k_{s,1}}{k_{s_{,2}}}\right) S_2} + \frac{\mu_{,1}\, s_1}{k_{s,2} + s_2 + \left(\frac{k_{s,2}}{k_{s_{,1}}}\right) S_1}$
Binary mixture, Non-competitive inhibition	$\mu = \frac{\mu_1 S_1}{(k_{s,1} + S_1)\left(1 + \frac{S_2}{k_{s,2}}\right)} + \frac{\mu_{,1}\, s_1}{(k_{s,2} + s_2)\left(1 + \frac{S_1}{k_{s_{,1}}}\right)}$
Binary mixture, uncompetitive enzyme inhibition	$\mu = \frac{\mu_1 S_1}{k_{s,1} + S_1\left(1 + \frac{S_2}{k_{s,2}}\right)} + \frac{\mu_{,1}\, s_1}{k_{s,2} + s_2\left(1 + \frac{S_1}{k_{s_{,1}}}\right)}$
SKIPb Binary mixture unspecified type of interaction	$\mu = \frac{\mu_1 S_1}{k_{s,1} + S_1 + I_{2,1} S_2}$

SKIP	$+\frac{\mu_{,2}\, s_2}{k_{s,2} + s_2 I_{1,2} S_1}$
Three compound mixture, unspecified type of interaction	$\mu = \frac{\mu_1 S_1}{k_{s,1} + S_1 + I_{2,1} S_2 + I_{3,1} S_3} + \frac{\mu_{,2}\, s_2}{k_{s,2} + s_2 + I_{1,2} S_1 + I_{3,2} S_3} + \frac{\mu_{,3}\, s_3}{k_{s,3} + s_3 + I_{1,3} S_1 + I_{2,3} S_2}$
Proposed by jiang et al.	$\mu = \frac{\mu_S}{k_s + S + \frac{s^2}{k_i} \frac{+s^3}{k_i}}$
Michaelis-MentenC	$v = \frac{VS}{k_m + S} or \frac{1}{v} = \frac{k_m}{Vmax} \frac{1}{S} + \frac{1}{Vmax}$
JD -factor	$JD = \frac{k_L}{G} \rho N s_c^{2/3} = k N_{Re}^{-(1-n)}$
Fick's Lawd	$\frac{d^2C}{dr^2} + \frac{2}{r}\frac{dC}{dr} = \frac{\rho_P}{De} v$
Thiele Moduluse	$\varphi = r_o \sqrt{\frac{k}{De}}$

Kp is a proportionality constant, and aR is the specific substrate consumption rate (mg/mg.hr) and ks is the saturation constant for substrate consumption (mg/l), respectively. F(i) depicts the functional relationship of the effect of metabolic intermediates on phenol degradation. The interaction parameter, bIij, shows how much substrate I influences substrate j's deterioration. v is the reaction's initial speed (in mg/s), Km is the Michaelis constant, and V m is the reaction's maximal speed in the case of catechol dioxygenase activity. ρp and De are the density of dried microbe (g/cm3) and effective diffusion coefficient of phenol within the bead, respectively. dC is the phenol concentration within the immobilised particles (mg/l), r is the radial position within the bead. The real rate of deterioration is v (mg/g/hr). The rate constant, k', is equal to kρp, where k is the fist-order degradation rate constant (cm3/g.hr), and er0 is the particle's radius.

6.2. TEMPERATURE MODELS FOR KINETIC PARAMETERS

There are fundamentally two types of treatment models for Monad maximum specific growth rate (1/h). The dependent variable is written as rate0.5 in square-root models and as ln rate in Arrhenius type models. The Arrhenius (1889) model's equation is

m = Ae - RT H* Equation 3

Where m is the monad maximum specific growth rate (1/h) and H * is the Arrhenius temperature characteristic (kJ/mol). It contains the generally assumed

constant temperature characteristic H*, however for microbial cultures, H* can vary by up to three or four times, depending on the temperature range utilised.

6.3. RESPONSE SURFACE METHODOLOGY (RSM)

RSM, is the most popular statistical method for optimising bioprocesses. It is a graphical statistical method and empirical modelling methodology that is used to assess the correlation between a number of experimental variables that can be controlled and the observed findings. Basically, this optimization approach entails three key steps: carrying out statistically planned trials, determining the coefficies in a mathematical model, and predicting the response and evaluating the model's suitability. Prior understanding of the procedure to produce a statistical model is necessary for response surface methodology, and takes the following form:

$$Y = f(x1, x2, x3, x4,..., xk) \quad \text{Equation 4}$$

The variable xi is coded for statistical calculations as $Xi = (xi - x0)/x$.

The following quadratic (second-degree) polynomial equation can be used to approximate how these variables respond mathematically:

$$Y = b0 + bi\ Xi + bii\ Xi2 + bi\ j\ Xi\ Xj \quad \text{Equation 5}$$

where Y represents the anticipated response, b0 the offset term, bi the linear effect, bii the square effect, and bij the interaction effect. The low, middle, and high values of each variable (equally spaced) are denoted by the numbers -1, 0, and +1, respectively. RSM was used by Annadurai et al. to optimise the medium composition for P.putida's phenol degradation (ATCC 31800).A mathematical model was then created to illustrate the impact of each medium composition and their interactions on the biodegradation of phenol. The mathematical expression of the relationship between phenol degradation and variables like glucose, yeast extract, ammonium sulphate, and sodium chloride was discovered. The response for the aforementioned variables may always be predicted by this model Taghreed al-khalid et al. (2012).

6.4. MASS TRANSFER

But the inherent development It is inferred that models for the dynamics of cells in suspension will also work well for biofilm cultures since kinetic models for phenol degradation in biofilms are complex and difficult to create. Kinetics degrade when the internal diffusion resistances are ignored. Despite its many advantages, the fundamental drawback of biomass immobilisation by entrapment is the limiting of product or nutrient diffusion caused by the resistance of the protective framework. The effectiveness of deterioration is usually decreased by a prevalent problem called diffusion limitation. The biomass is not easily accessible to contaminants because the majority of locations will be inside the bead. A support material should be strong, chemically inert, and inexpensive to efficiently immobilise biomass. It should have a strong connection to the cells, a large capacity for loading, and a flexible structure to allow for minimal restriction on diffusion.

For any phenol biodegradation process in a moving bed reactor using immobilised biomass, there are three basic steps that occur in the bioreactor:

1) the movement of oxygen into the liquid phase from the gas phase.
2) moving phenol, oxygen, and other nutrients from the bulk liquid phase to the biofilm's surface; and
3) the biofilm's phenol, oxygen, and other nutrients diffuse and react at the same time.

The final step (3), which is a molecular phenomenon, is independent of the reactor's flow parameters or turbulence.100 When it comes to the first process (1), dissolved oxygen is a key factor. Oxygen transfer restrictions can cause insufficient oxygen to have an impact on phenol biodegradation.

If oxygen were utilised instead of air, there would be five times increase in the oxygen mass transfer rate. Alternately, increasing stirring speed correspondingly improved phenol decomposition and increased the mass transfer coefficient of oxygen.

In step (2), the substrate is thought to be transferred into the biofilm in two steps:

- the substrate's transition from bulk liquid to a bioparticle's surface; and
- Diffusion through the layer of microorganisms (biofilm).

Numerous research have concentrated on this process since the speed at which phenol is transported from the bulk phase to the biofilm's surface would directly affect the biochemical reaction taking place there. The design and modelling of bioreactors must therefore take into account external mass transfer coefficients for the transport of phenol from the bulk phase to the surface of the biofilm.

7. CONCLUSION

Phenolic compounds must be eliminated as priority pollutants in order to maintain environmental quality. Since biological treatment is the most successful, cost-effective, and ecologically friendly technology now available, it is receiving more and more attention in the field of pollution control. The basic function of microbial metabolism is energy conversion, and it is controlled by enzymatic systems in which reaction intermediates are important. In addition, numerous models have been put forth in order to better understand the kinetics of phenols' biodegradation. The Haldane and Monod models are most frequently employed. The effectiveness of the biodegradation process is significantly influenced by the mass transport mechanisms and regimes.

8. FUTURE SCOPE AND DIRECTIONS

Development efforts should focus on novel types of bioreactors targeting practical utilization and efficient long-term performance. It is essential to develop and design efficient reactors that would reduce mass transfer limitations and enhance the degradation rate. Novel processes are required as well.

CREDIT AUTHOR STATEMENT

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CONFLICT OF INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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