KINETICS OF BIOLOGICAL TREATMENT OF PESTICIDE WASTEWATER

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ABSTRACT

Pesticides are chemical substances intended to protect food crops and livestock from pests in order to promote agricultural productivity and protect public health. Contamination of soil, air and water and threat to human and animal health are the major constraints in the use of pesticides. Treatment of pesticide contaminated water is, therefore, paramount. Biological treatment provides the most economical option when compared with other treatment methods. The aim of the study was to develop a safe and effective farm biological treatment for low level agricultural pesticide wastewater. In this study, the degradation of the fungicide captan was evaluated under batch and continuous modes of operation with a retention time of 15 days. The results showed that the initial cell number (30.1×10^6 cells/mL) in the soil water mixture first declined with time during the first 24 hours reaching 15.6×10^6 and 11.1×10^6 cells/mL in the batch and continuous bioreactors, respectively. This was due to the inhibitory effect of pesticide on some of the soil microbial species that had less tolerance to captan at the initial concentration of 144 mg/L. Then, the microbial population started growing, reaching its maximum after 5 and 12 days in the batch and continuous bioreactors, respectively. The lag period and the specific growth rate for the batch bioreactor were 22 h and 0.096 h^{-1}, respectively. A captan degradation efficiency of 89.6% was achieved after 10 days in the continuous bioreactor compared to a degradation efficiency of 100% after 5 days in the batch bioreactor. This study showed that the effluent from the continuous bioreactor had a captan concentration of 12 mg/L which is not acceptable for livestock drinking water. A half life of 52 h was observed in the batch bioreactor.

Keywords: *Pesticide, Captan, Biodegradation, Bioreactor, Soil microbes, Specific growth rate, Inhibition, Half-Life Time.*

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INTRODUCTION

Pesticides provide the primary means for controlling organisms (fungi, bacteria, mites, insects, nematodes, rodents and undesirable plants) that compete with man for food and fibre or cause injury to man, livestock and crops. They are classified based on the pest they control into several classes: fungicides, bactericides, acaricides, insecticides, nematicides, rodenticides and herbicides. The worldwide pesticide expenditures in 2007 were 39.4 billion dollars accounting for 2.37 billion kg of pesticide. Pesticide expenditures account for 13-22% of the total cost of production per hectare (Horowitz and Lichtenberg, 1993). Osteen and Livingstion (2006) reported that for every dollar spent on pesticide farmers receive an additional of $4-33 in revenue from increased yield, depending upon crop rotation and year of production.

Pesticides play a vital role in increasing agricultural production and permitting the economic production of wide ranges of vegetable, fruit, cereal, forage, fibre and oil crops which now constitute a large part of successful agricultural industry in many countries. They lower crop losses, increase revenue to farmers because of the additional marketable yield obtained with their use and thus lower the cost of production per unit output (Horowitz and Lichtenberg, 1993). Other benefits of pesticides include: (a) reducing uncertainty of crop loss from pests, (b) increasing profit to farm input suppliers (machinery, fertilizer, chemicals and seed companies) from increased sale, (c) benefiting consumers through decreased price of raw foods or improved quality of food products and (d) benefiting society as whole (farmers, consumers, farm suppliers, food processors) from increased employment opportunities and expanded export of food products (Oerke and Dehne, 2004; Cooper and Dobson, 2007).

However, pesticides are toxic chemicals and if not managed properly can adversely affect people, pets, livestock, wildlife and desirable plants in addition to the pests they are intended to destroy (Centner, 1998; Wilson and Tisdell, 2001). Pesticide residues remain in the containers and application equipment after pesticides are applied to target areas. These residues are removed from applicators by rinsing with water resulting in

the formation of a toxic wastewater that represents a disposal problem for many farmers (Kearney et al., 1988). Currently, disposal of pesticide wastewater is carried out by several methods including (a) land cultivation, (b) dumping on land, in ditches, in lagoons and in soil pits, and in extreme cases in sewers and streams near the rinsing operation, (c) use of evaporation ponds and (d) land filling (Al hattab and Ghaly, 2012). These methods of disposal are totally unsafe, as the surface run off will reach streams, rivers and lakes and the infiltration of the wastewater into the local soil will eventually end up in ground water. The ecological impact of unsafe disposal of pesticides can be significant depending on the type and concentration of pesticides in the wastewater.

Therefore, pesticide containing wastewater must be properly treated. The treatment methods currently used for pesticide containing wastewater include (a) incineration, (b) chemical treatment such as O_3/Uv oxidation, Fenton oxidation and hydrolysis (c) physical treatment using inorganic and organic absorbents and (d) biological treatment such as phytoremediation, composting and bioaugmentation. These treatment methods either require land or are expensive and suffer from variability of effectiveness (Winterlin et al., 1989; Al hattab and Ghaly, 2012).

The aim of the study was to develop a safe and effective on farm biological treatment for low level agricultural pesticide wastewater and to evaluate its mode of operation (batch vs. continuous).

EXPERIMENTAL APPARATUS

The pesticide treatment system (Figure 1) consisted of pesticide contaminated wastewater feeding system, 2 bioreactors (batch and continuous) and 2 effluent collection tanks.

Bioreactors

Two identical bioreactors (each of approximately 15.7 L volume) were constructed from Plexiglas material and designed to hold 10L each of soil-water- pesticide mixture plus ahead space. Each bioreactor was constructed of 1.0 cm thick Plexiglas cylinder of 20 cm diameters and 50 cm height. The bottom of the cylinder was made of 1.0 cm thick circular Plexiglas plate of 20 cm diameter which was glued to the cylinder. The top lid was made of 1.0 cm thick circular plate of 22 cm diameter which was secured into the cylinder using six stainless steel screws and wing

nuts. The lid had three 1.5 cm diameters holes: one in the center for the mixing shaft and the other two holes were used for the wastewater input and air exhaust.

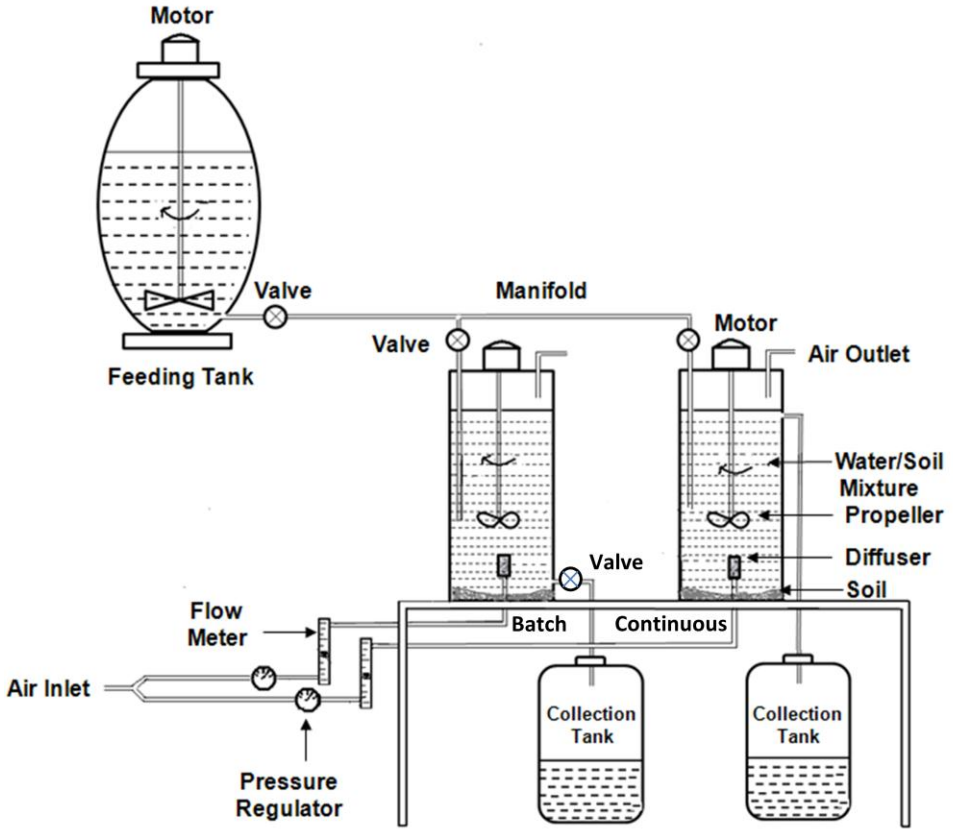


Figure 1: Experimental apparatus.

The reactor contents were mixed using as 55 rpm induction motor (Japan Servo Company, Tokyo, Japan) which was mounted on the reactor lid and connected to a 1.5 cm diameter mixing shaft. A 15 cm diameter propeller was placed on the shaft at 2 cm from the diffuser. An air inlet port was provided at the bottom of each cylinder and was fitted with 20 mm PVC elbow. An air diffuser (Dynamic Aqua-Supply Ltd., Sydney, Nova Scotia, Canada) was attached to the elbow inside the cylinder. The diffuser diameter and height were 15 and 25 mm, respectively. The other end of the elbow was connected to Tygon tubing which connected the diffuser to the air supply unit that consisted of an air compressor (3/4 HP Shanborn

model MCIFC 75-715, DV Systems Maritimes, Halifax, Nova Scotia, Canada), a pressure regulator (Model ZFMQ000PR, Millipore Pressure Regulator, Etobicoke, Ontario, Canada) and a flow meter (Model 60648, Cole Parmer, Chicago, Illinois, USA).

Feeding System

The wastewater feeding system consisted of storage tank and a distribution manifold with a set of three values. A 100 L plastic tank was used to store the wastewater. The tank was fitted with a stirring paddle driven by a 1/12 HP electric motor (Model 5SCP10FG17AX, General Electric, Mississauga, Ontario, Canada) mounted on the tank cover. A feeding and ventilation ports were also provided on the tank cover. A 5 cm ball valve was connected to the fitting on the tank from one side and to the manifold from the other side. The other two valves on the manifold controlled the flow into the bioreactors.

Collection Tanks

Two 25 L plastic carboys (Cat No.02-961B) Fishers Scientific, Montreal, Quebec, Canada) were used to collect the effluent from the bioreactors.

EXPERIMENTAL MATERIALS

Pesticide

The fungicide Captan 80-WP ($C_9H_8ClNO_2S$) was chosen for this experiment because it is one of the most heavily used pesticide. The properties and structure of Captan 80-WP are shown in Table (1). It is classified as a protectant eradicant fungicide and is one of the most used pesticides today due to its effectiveness in controlling a wide variety of fungal diseases (Table 2). The formulation of this pesticide is a microfine wettable powder containing 80% active ingredient (75.5% N-[trichloromethyl)thio]-4-cyclohexene-1,2-dicarboaimide and 4.3% related derivatives). The balance (20%) is made of mineral dust and wetters dispersants. This formulation is preferred by many growers since it minimizes visible residue and thus provides an excellent vegetable and fruit finish.

Soil

The soil used in this experiment was obtained from an agricultural field that receives urea, NPK fertilizers and liquid manure. The top trash coves of the soil was scraped away and the soil was removed by a shovel from

the top 30 cm and placed in a heavy duty (16 m thick) Polyethylene bag and transported to the laboratory. The soil was used as a source of mixed microbial culture.

Table 1: Chemical formula and structure for captan (Wolfram Alpha, 2011; Sigma Aldrich, 2011).

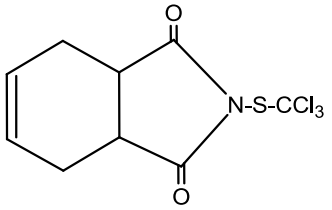
Chemical Name	Properties	Structure
3a,4,7,7a-tetrahydro-2-[{tricholoromethylthio}]-1H-isoindole-1,3(2H)-dione	Powerful protectant fungicide Solid (yellow amphous powder) Insoluble in water Molecular Weight= 300.59 g/mol Boiling Point = 314°C Melting Point = 172°C Density = 1.74g/mL Flash Point = 143°C Carcinogen Moderate eye irritant Skin sensitizer Toxic by inhalation No evidence of phototoxicity	 $C_9H_8Cl_3NO_2S$

Table 2: Crops and fungal diseases registered for Captan 80-WP.

Crop	Fungal Diseases Treated
Apple	Scab, Sooty Bloch, Fly Speck, Brook's Spot, Bitter Rot, Black Rot, Bull's Eye Rot
Apricot	Brown Rot
Cherries	Brown Rot, Leaf Spot
Peach	Brown Rot, Scab
Pear	Scab, Sooty Bloch
Plum	Black Rot, Brown Rot
Grape	Dead Arm, Dawny Mildew, Black Rot
Raspberry	Fruit Rot
Blackberry	Fruit Rot
Loganberry	Cane Spot, Fruit Rot, Leaf Spot, Spur Blight
Blueberry	Fruit Rot, Mummy Berry
Strawberry	Gray Mold Rot, Leaf Spot
Rhubarb	Leaf Rot
Cucumber	Anthracnose, Scab
Tomato	Anthracnose, Septoria, Leaf Spot

EXPERIMENTAL PROCEDURE

Experimental Protocol

Two experiments were carried out: a batch experiment which was run for 15 days and a continuous experiment which was run with a retention time of 15 days. Eighteen grams of Captan dust (14.4 g active material) were

added into the water (100L) in the feeding tank to provide a Captan concentration of 144mg/L in the wastewater. The initial soil:water ratio in the bioreactors was 1:3. The soil (0.75 L) was placed in the bioreactors and the water (2.25 L) was then added. The batch bioreactor was filled up to the 10 L level. For the continuous bioreactor, the feeding pump was adjusted to provide a flow rate of 0.46mL/minute in order to achieve the 15 day retention time. The mixing motor and the air compressor were turned on. The air flow rate was set at 10 L/min (1v/v/min) using the flow meter. Samples were collected from each bioreactor on a daily basis and vacuum filtered using a coarse filter paper (P8 Grade, FisherScientific, Montreal, Quebec, Canada) to remove any soil particles. The filtered samples were used for microbial (plate count) and pesticide analyses.

Plate Count Analysis

The plate count was performed on the initial soil water mixture before the addition of pesticide and on the samples collected from the bioreactors. For each sample, 5 test tubes were filled with 9.9 ml of peptone solution. A 1:100 dilution was prepared by pipetting 0.1mL of the initial dilution into the first tube. This was then mixed well and 0.1 mL was placed on an agar lined Petri dish and spread over the entire surface using a glass wand. The wand was cleaned with reagent alcohol and flamed before each use. From the diluted tube, 0.1 mL was transferred to another tube contains 9.9 mL peptone solution to produce a dilution of 1:1000. The mixture was mixed well and 0.1 mL was transferred into another Petri dish. The same procedure was repeated to produce final dilutions of 1: 100, 1:1000, 1:10000, 1:10000, 1:100000 and 1:1000000. Three plates of each dilution were carried out. All the inoculated Petri dishes were then placed in a temperature control incubator (Model 2020, Sheldon Manufacturing Inc, Cornelius, Oregon, USA) at 35°C. The plates were examined after 24h and the dilution that produced reasonable countable number of calories were selected. The total colonies on each Petri dish were calculated using a plate counter (Model 7-901, Fisher Scientific, Montreal, Quebec, Canada). The population was then determined by multiplying the number of colonies by the dilution factor.

Pesticide Analysis

Three ml of the sample were mixed with 3 mL of the hexane/ether solvent (95:5) in a test tube. The test tube was then caped and heated at 115 °C

for 30 min followed by a cooling period to a temperature below 0°C. When the sample was frozen, the liquid solvent was withdrawn from the top. 2 µL of this sample were then used for injection into a gas chromatographer (5890 series II, Hewlett Packard, California, USA). The initial and final concentrations of captan in each unit were determined. The chromatograph was calibrated by injecting 1.0 µL of the extracted captan mixture into the 25 m × 0.2 mm capillary column.1.0 µL of the extracted sample was then injected into the column. The column temperature was first maintained at 40°C for three minutes and then increased at the rate of 10 °C per minute until a temperature of 270°C was attained. The column was then maintained at 270 °C for five minutes. The injection port was set at 25°C while the flame ionization detector was set at 250 °C. Helium was used as a carrier gas at a flow rate of 1.2 mL/min.

RESULTS AND DISCUSSION

Microbial Growth

The growth of the mixed microbial population in the batch and continuous bioreactors is shown in Figure 1. The initial cell number in the soil water mixture in both bioreactors (batch and continuous) was 30.1×10^6 cells/mL. The number of cells first declined with time during the first 24 hours reaching 15.6×10^6 cells/mL in the batch bioreactor and 11.1×10^6 cells/mL in the continuous bioreactor and then increase gradually in both reactors. This was due to the inhibitory effect of pesticide on some of the soil microbial species that had less tolerance to captan at the initial concentration of 144 mg/L. The lower value (29% lower) observed in the continuous bioreactor compared to that of the batch bioreactor was due to the loss of microbes from that bioreactor with the effluent.

Similar results were reported by several authors for captan. Wainwright and Pugh (1975) reported declined trend of bacterial population (from 16.5×10^6 to 14×10^6cells) during first 48 hours after application of 25µg/g captan to field soils. Agnihotri (1971) reported a significant reduction (from 2.3×10^5 to 0.4×10^5cells) of the actinomycete population in fresh soil by the 7^{th} day after application of 125 ppm captan. Martínez-Toledo et al. (1998) studied the effects of captan concentration (2.0-10.0 kg/ ha) on microbial function in four agricultural soils under aerobic conditions and reported significant decreases in total culturable fungal populations, nitrifying bacteria and aerobic nitrogen fixing bacteria

during the first 14 days. Piotrowska-Seget et al. (2008) reported 46% reduction (from 7.8×10^5 to 4.2×10^5) in bacterial population during the first 10 days after application of captan at a rate of 8.5 mg/g of soil and observed increase (from 4.2×10^5 to 7.6×10^5) in population after 94 days which was about 97.43% of the original population. Similar results were also reported for other pesticides such as malathion (Shan et al., 2009), chlorpyrifos alone and in combination with chlorothalonil (Xiaoqiang et al., 2008), dichlorvos (Ning et al., 2010), 2-(2-methyl-4-chlorophenoxy) propionic acid (MCPP) (de Lipthay et al., 2003; Tuxen et al., 2006), phenoxy acids (Chilton et al., 2005), 2,4-D (Broholm et al., 2001), 2-(2,4-dichlorophenoxy) propionic acid (de Lipthay et al., 2003).

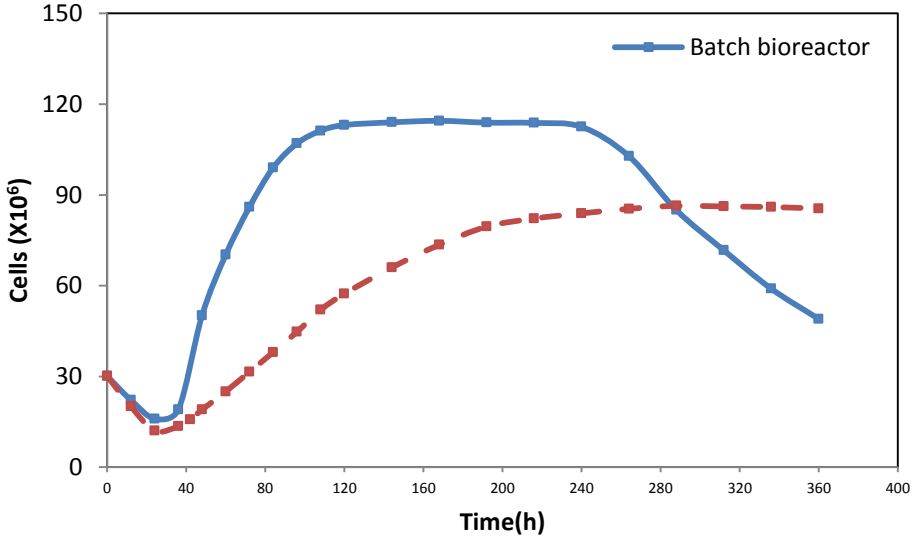


Figure 1: Microbial growth

The four microbial growth phases normally encountered in a batch operation (lag, exponential growth, stationary growth and death phases) were observed in the growth curve of the batch bioreactor. After the initial lag period, the microbial population in the batch bioreactor started to increase with time reaching a maximum of 113.9×10^6 after 120 h (5 days from the start), remained relatively constant till the 240 h (for 5 days) and then started to decline. The microbial population of the continuous bioreactor also increased but at a slower rate than that of the batch bioreactor due to the continuous loss of microbes from the bioreactor with the effluent. It reached a steady state condition (when the

rate of microbial growth in the bioreactor was equal to the rate of microbial loss from the bioreactor with the effluent) after 288 h. The microbial population in the continuous bioreactor at the steady state was 86.5×10^6 cells/mL (75.94% of that in the batch reactor).

The lag period and specific growth rate were determined from the batch operation data according to the procedure described by Ghaly et al. (1989) as shown in Figure 2. The lag period and the specific growth rate were 22 h and 0.096 h^{-1}, respectively. Radianingtyas et al. (2003) reported 18 h lag period and 0.014 h^{-1} specific growth rate while degrading 4-choloroaniline (1 mM) in a batch reactor with a bacterial consortium comprising of four different species isolated from an Indonesian agricultural soil. Lappin et al. (1985) reported 18 h lag period and 0.09 h^{-1} specific growth rate while degrading mecoprop (1 gm/L) in a batch reactor with a microbial community isolated from wheat root systems. Rhee et al. (1997) were able to demonstrate pyridine degradation (3 mM) in a batch reactor and reported 13 h lag period and 0.08 h^{-1} specific growth rate using denitrifying bacteria isolated from industrial wastewater.

The lag period and net specific growth rate (μ_{net}) was also determined for the continuous bioreactor during the initial unsteady state period using the same procedure as shown in Figure 3. The lag period and net specific growth rate for the continuous bioreactor were 26 h and 0.045 h^{-1}, respectively. Krishna and Philip (2009) conducted studies on biodegradation of carbofuran at a concentration of 150 mg/L in a continuous reactor and reported 48 h lag period and 0.3928 d^{-1} specific growth rate using carbofuran enriched cultures.

The net specific growth rate (μ_{net}) in the continuous bioreactor is defined as follows:

$$\mu_{net} = \mu - k_r \quad (1)$$

Where:

μ = Specific growth rate (h^{-1})

μ_{net} = Net specific growth rate (h^{-1})

k_r = The cell removal rate with effluent (h^{-1})

The results indicated that the rate of microbial loss with the effluent (k_r) was 0.051 h^{-1}.

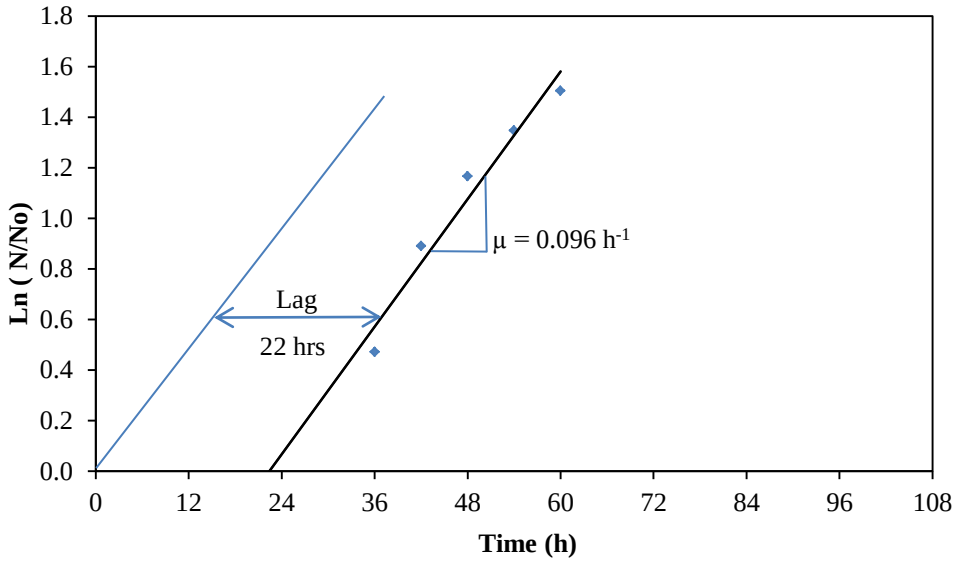


Figure 2: Determination of the lag period and specific growth rate in the batch bioreactor.

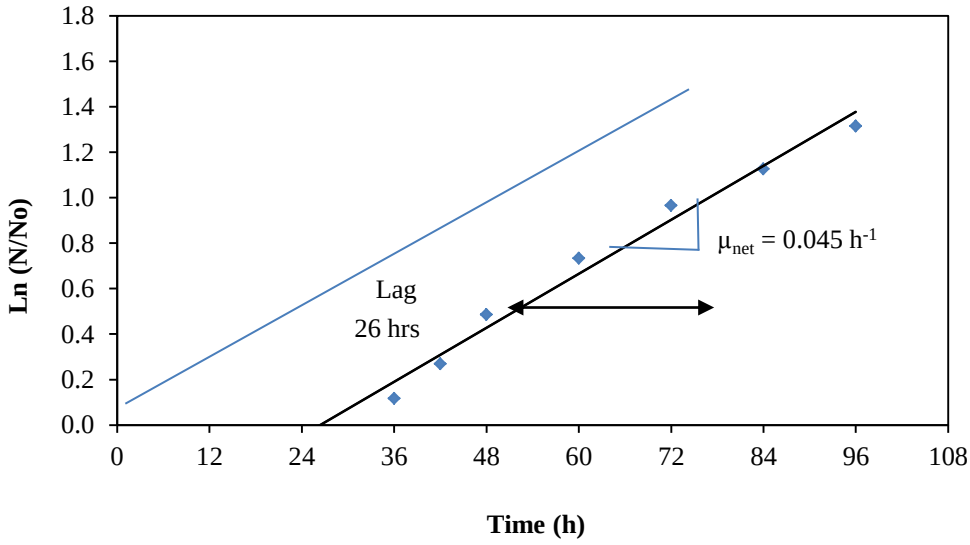


Figure 3: Determination of the lag period and net specific growth rate in the continuous bioreactor.

Pesticide Degradation

The pesticide concentrations in the effluent samples taken from the batch and continuous bioreactors overtime are shown in Figure 4. The pesticide concentration in the batch bioreactor started to decline with time reaching zero value after 120 h (5 d) from the start. Also, the pesticide

concentration in the effluent of the continuous bioreactor declined with time reaching a constant value of 15 mg/L after 288 h (10 d). Thus, a removal efficiency of 89.6% was achieved after 10 days with the continuous bioreactor compared to a removal efficiency of 100% after 5 d with the batch bioreactor. Megadi et al. (2010) reported a complete degradation of fungicide captan after 6 days during growth of *Bacillus circulans* in the mineral salt medium (MSM) containing 0.1% captan. Buyanovsky et al. (1988) reported 33% degradation of captan (with an initial concentration of 50 mg/L) after 2 weeks (including lag phase of 2 days) of incubation with soil bacteria, no further degradation of captan was observed after the 2 weeks period. The maximum permissible value for captan and metabolites in livestock water is set 13 µg/L. The batch bioreactor used in the study achieved 100% removal of captan, while the effluent from continuous bioreactor contained 15 mg/L which is not acceptable for livestock water.

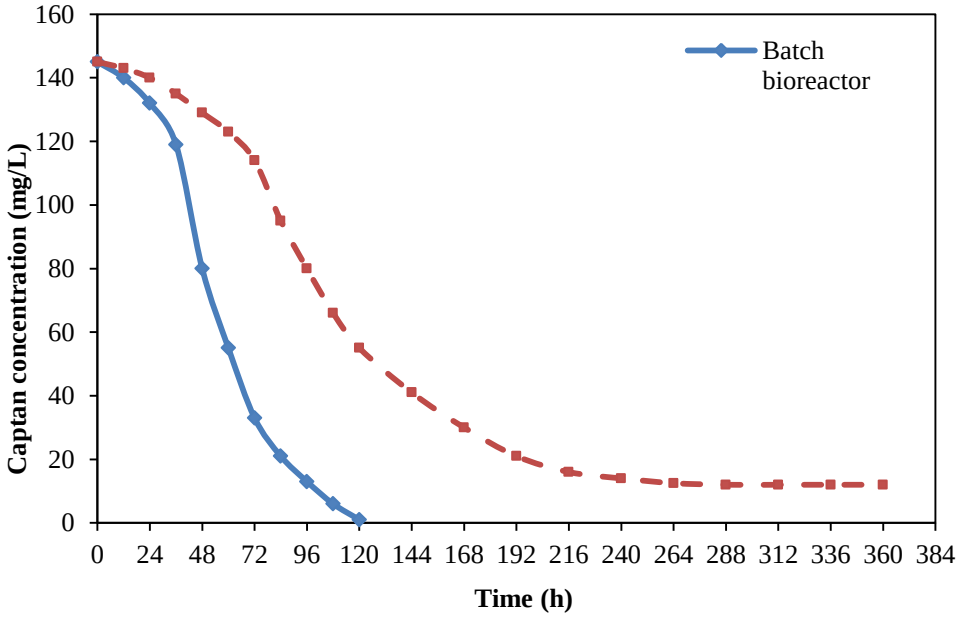


Figure 4: Pesticide concentration in batch and continuous bioreactors

Biological degradation of pesticides refers to the use of microorganisms to destroy those chemicals in solid or liquid wastes into harmless by

products. The aerobic biological treatment relies on microbial activity and aeration efficiency. Microbes that naturally occur in soil increased significantly in number and began to biodegrade pesticide in this study. The microbes utilized the pesticide as bioavailable carbon source for energy (respiration) and synthesis (growth) of microbial cells according to the following equations:

Energy

$$\text{Organic matter} + O_2 \xrightarrow{Microbes} CO_2 + H_2O + \text{other products} + \text{Heat} \quad (2)$$

Synthesis

$$\text{Organic matter} + NH_4 \xrightarrow{Microbes} \text{more microbes} \quad (3)$$

The proposed pathway for the degradation of captan is shown in Figure 5. The soil microbial population used in this study contained microorganisms capable of utilizing the carbon, chloride, nitrogen and sulphur found in captan ($C_9H_8Cl_3NO_2S$) under aerobic condition into carbon dioxide (CO_2), water (H_2O), chloride (Cl), nitrate (NO_3) and sulphate (SO_4) and obtain the energy required for growth according to the following equations (Swanner and Templeton, 2011; Megadi et al., 2010; Munch et al., 1996).

$$C_9H_8Cl_3NO_2S + 8.5O_2 \xrightarrow{Soil\ microbes} 9CO_2 + H_2O + 3HCl + NH_3 + H_2S + \Delta E \quad (4)$$

The captan degradation process takes place in several steps. In the first step, captan is converted into *cis*-1,2,3,6-tetrahydro phthalimide, thiocarbonyl chloride and hydrochloric acid. In the second, step c*is*-1,2,3,6-tetrahydro pthalimide is converted into *cis*-1,2,3,6-tetrahydro pthalimidic acid and thiocarbonyl chlorides converted into H_2S, CO_2 and H_2O. In the third step, the *cis*-1,2,3,6-tetrahydro pthalimidic acid is converted into O-phthalic acid and ammonia. In the forth step, the O-phthalic acid is converted into protocatechuic acid. In the fifth step, the protocatechuic acid is converted into 3- carboxy-*cis, cis* muconic acid which is oxidized to CO_2 and H_2O.

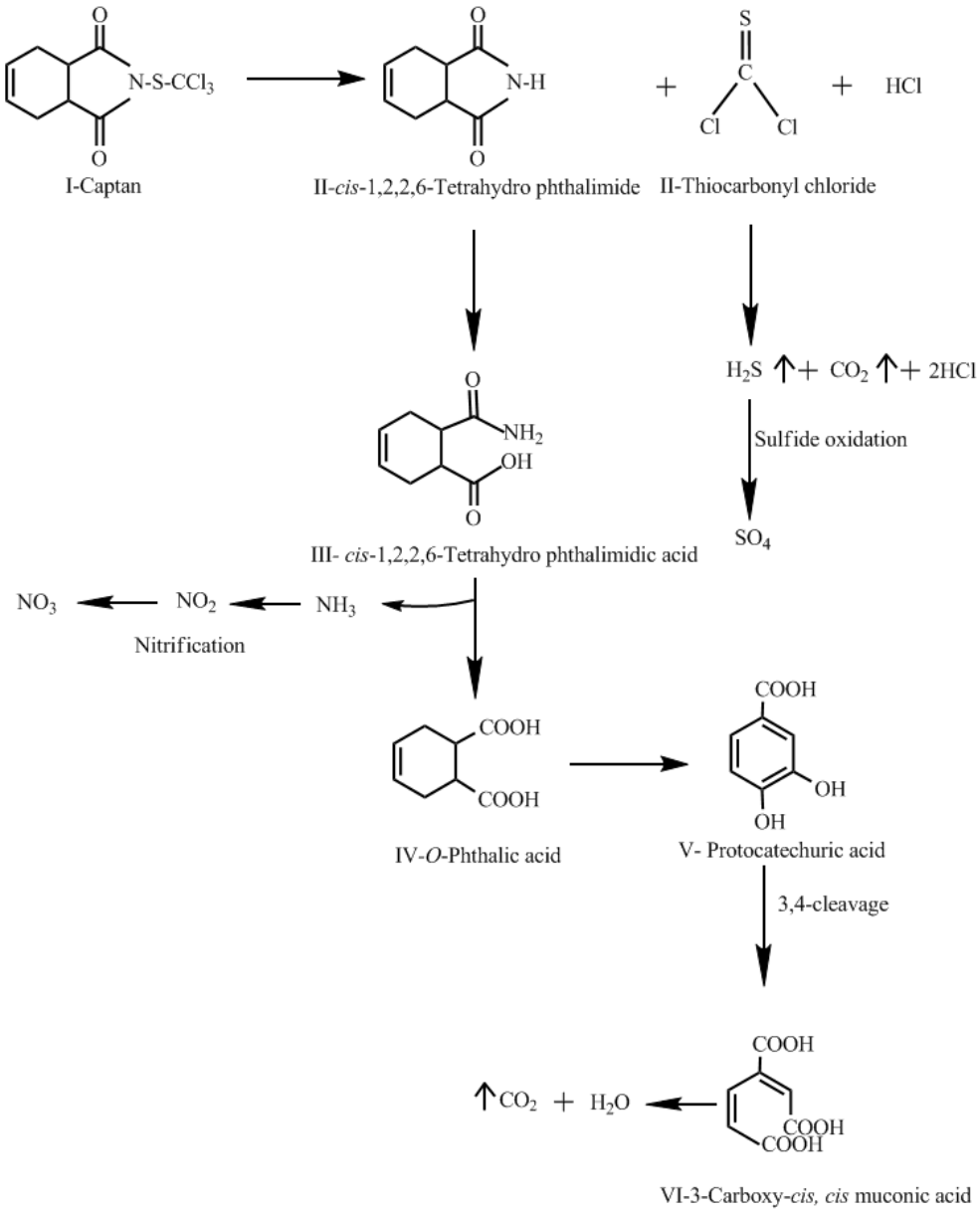


Figure 5: Pathway for the degradation of fungicide captan under aerobic condition (Modified from Megadi et al., 2010).

The NH_3 is converted into NO_3 by the nitrifying bacteria while the H_2S is converted into SO_4 by the hydrogen sulphide reducing bacteria.

$$NH_3 + 2O_2 \xrightarrow{Nitrifiers} NO_3^- + H_2O + H^+ + \Delta E \quad (5)$$

$$H_2S + 2O_2 \xrightarrow{Hydrogen\ sulfide\ reducing\ bacteria} SO_4^{-2} + 2H^+ + \Delta E \quad (6)$$

The biodegradation of organic substrates such as pesticides in a batch system can be described by the following equation.

$$P_t = P_o e^{-kt} \quad (7)$$

Where:

P_t = Concentration of pesticide at the time t (mg/L)
P_o = Initial concentration of pesticide (mg/L)
k = Rate constant (h^{-1})
t = Time (h)

A plotting of ln (P_t/P_0) versus time (t) yields straight line with a slope equals k. However, plotting the data obtained from the batch bioreactor did not fit a straight line for the entire period. The results (Figure 6) showed different degradation rates for the lag period (0.0025 h^{-1}) and exponential growth period (0.71 h^{-1}). It appears from the results that the microorganisms are able to utilize captan as a source of carbon and energy for maintenance during the lag period. Karpouzas et al. (2005) reported 25% degradation of cadusafos (at an initial concentration of 12 mg/L) during the lag period of 30 h after inoculation of *Flavobacterium* sp. and *Sphingomonas* sp. (isolated from cadusafos contaminated soil) which was followed by gradual increases in bacterial populations (reaching 3×10^6 and 8×10^6 cells/mL for the *Flavobacterium* and the *Sphingomonas* sp. in 72 h , respectively) that resulted in complete degradation of cdusafos by both isolates in 78 h. Karpouzas and Walker (2000) reported a 30% degradation of ethoprophos (initial concentration of 100 mg/L) after inoculation of *Pseudomonas putida* (isolated from ethoprophos contaminated soil) with a mineral salts medium supplemented with nitrogen (MSMN) in the first 33 h and observed complete degradation after 50 h. In this study, 8.2% (12 mg/L) of the

captan in the batch bioreactor was degraded during the lag period of 22 h and complete degradation was achieved in 120 h.

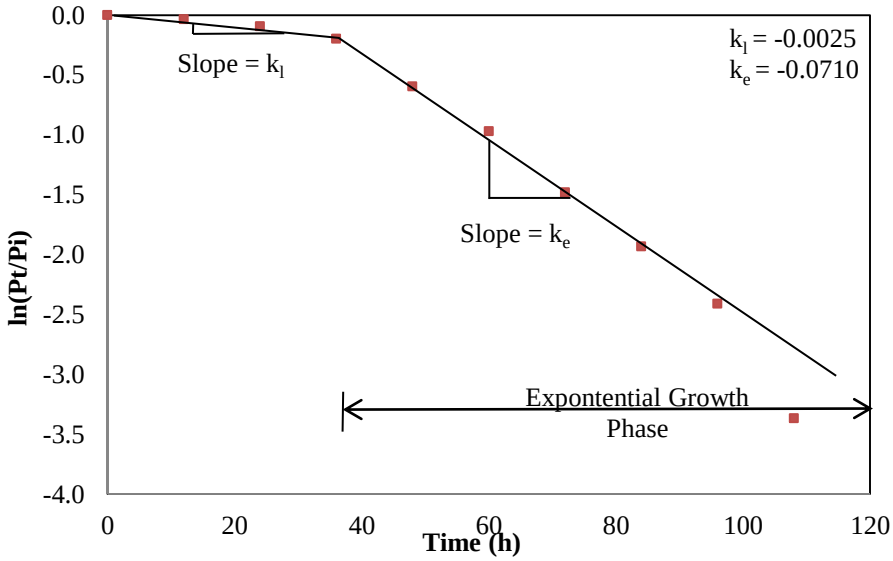


Figure 6**:** Determination of rate constant k.

The captan half-life observed for the batch bioreactor in this study was 52 h. Leoni et al. (1992) reported a captan half-life of 3.6 days in an activated sludge system, Hermanutz et al. (1973) reported captan half-life of 7 h at 12 ºC and 1 h at 25 ºC in Lake Superior. Ghaly et al. (2007) reported primiphos-methyle half life of 25 h in composting system (at 50-60ºC). In this study, a captan half life of 52 h was observed for the batch bioreactor.

CONCLUSIONS

The initial cell number (30.1×10^6 cells/mL) in the soil water mixture was first declined with time during the first 24 hours reaching 15.6×10^6 and 11.1×10^6 cells/mL in the batch and continuous bioreactors, respectively. This was due to the inhibitory effect of pesticide on some of the soil microbial species that had less tolerance to captan at the initial concentration of 144 mg/L. The results indicated that microbial population reached its maximum after 5 and 12 days from the start in batch and continuous bioreactors, respectively. The lag period and the specific growth rate for the batch bioreactor were 22 h and 0.096 h^{-1}, respectively. Captan degradation efficiency of 89.6% was achieved after

10 days in the continuous bioreactor compared to a degradation efficiency of 100% after 5 days in the batch bioreactor. A half life of 52 h was observed in the batch bioreactor. This study showed that the batch mode of operation completely removed captan while the effluent from the continuous bioreactor had a captan concentration of 12 mg/L which is not acceptable for livestock drinking water.

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الملخص العربى

حركية المعالجة البيولوجية لمياه الصرف الصحي بالمبيدات

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المبيدات هى عبارة عن أي مادة كيميائية تستخدم بغرض وقاية النباتات من الأمراض والأفات من أجل تحسين جودة وانتاجية الحاصلات الزراعية والحصول على انتاج زراعي سليم مع الحفاظ على الصحة العامة. يمثل تلوث التربة والهواء والماء والتأثير السلبي على صحة كل من الانسان والحيوان أحد أهم الأسباب التي تتعارض مع استخدام المبيدات على نطاق واسع. وبالتالي فان عملية معالجة المياه من المبيدات الملوثة هام جدا للحد من التأثير السلبي للمبيدات على البيئة. تعتبر عملية المعالجة الحيوية للمبيدات من أرخص طرق المعالجة مقارنة بطرق المعالجة الأخرى. وبالتالي تهدف الدراسة الى ايجاد وتحسين وسيلة مزرعية حيوية فعالة وأمنة لمعالجة مياه الصرف الزراعي الملوثة بالمبيدات. في هذه الدراسة تم تقييم عملية التحلل الحيوي لمبيد الكابتان (captan) المستخدم فى مقاومة الفطريات تحت ظروف التشغيل المستمر وظروف التشغيل على دفعات بعد زمن استبقاء قدره ١٥ يوم. اشارت النتائج الى تناقص التركيز الابتدائي للخلايا الميكروبية (٣٠.١ × $١٠^{٦}$) فى خليط التربة والمياه خلال فترة الـ ٢٤ ساعة الأولى ليصل الى تركيز ١٥.٦ × $١٠^{٦}$ و ١١.١× $١٠^{٦}$ خلية ميكروبية فى حالة ظروف التشغيل على دفعات وظروف التشغيل المستمرة، على التوالي.

***مدرس الهندسة الزراعية ـ كلية الزراعة ـ جامعة القاهرة.**

تناقص الخلايا الميكروبية كان نتيجة التأثير المثبط للمبيد على بعض أنواع الخلايا الميكروبية التي لها قدرة أقل لتحمل التركيز الابتدائي (١٤٤ مجم/لتر) لمبيد الكابتان (captan). بعد الـ ٢٤ ساعة الأولى بدأ تركيز الخلايا الميكروبية فى الزيادة ووصل النمو الميكروبي الى أقصى قيمة بعد ٥ و١٢ يوم لظروف التشغيل على دفعات وظروف التشغيل المستمر، على التوالي. تم حساب كل من زمن التأخير ومعدل النمو النوعي ووجد يساوي ٢٢ ساعة و ٠.٠٩٦ ساعة$^{-1}$، على التوالي بالنسبة لظروف التشغيل على دفعات. تم الحصول على كفائة تحلل للمبيد مقدارها ٨٩.٦% بعد فنرة زمنية قدرها ١٠ أيام تحت ظروف التشغيل المستمر بالمقارنة بكفائة تحلل حيوي مقدارها ١٠٠% بعد فترة زمنية مقدارها ٥ أيام تحت ظروف التشغيل على دفعات. نصف العمر لمبيد الكابتان (Captan) وجد يساوي ٥٢ ساعة تم حسابها تحت ظروف التشغيل على دفعات. أشارت الدراسة الى أنه تحت ظروف التشغيل على دفعات يمكن ازالة المبيد بالكامل ةالحصول على كفاءة تحلل ١٠٠% بينما تحت ظروف التشغيل المستمر وصل التركيز النهائي للمبيد الى ١٢ مجم/لتر. تركيز ١٢ مجم/لتر يعتبر قيمة غير مقبولة بالنسبة لمياه الشرب للحيوانات والماشية طبقا للمعايير القياسية.