EFFECTS OF Ni(II) ON BOD EXERTION - MODELLING OF THE BOD CURVE

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Prof. Dr. Alpay ANKARA
Director

I certify that thesis satisfied all the requirements as a thesis for the degree of Master of Science in Environmental Engineering Department.

Prof. Dr. Gülerman SÜRÜCÜ
Chairman of the Department

We certify that we have read thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science in Environmental Engineering Department.

Asst.Prof.Dr. Ülkü YETİŞ
Supervisor

Examining Comittee in Charge:

Prof.Dr. Celal Ferdi GÖKÇAY (Chairman)
Assoc.Prof.Dr. Coşkun YURTERİ
Assoc.Prof.Dr. Mustafa OĞUZ
Assoc.Prof.Dr. Figen ERKOÇ
Asst.Prof.Dr. Ülkü YETİŞ

ABSTRACT

EFFECTS OF Ni(II) ON BOD EXERTION - MODELLING OF THE BOD CURVE

YÜCEL, Gamze
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Supervisor: Asst.Prof.Dr. Ülkü YETİŞ
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In this study, the toxic effect of Ni(II) on BOD was evaluated and the BOD exertion in the presence of Ni(II) was modelled. To this purpose, different concentrations of Ni(II) (1.0, 2.0, 3.0, 4.0, 5.0 and 10.0 mg/L) were added to a synthetic wastewater sample, and the daily BOD exertions were measured for a period of 20 days. As it was expected; a gradual decrease was observed in the BOD values with increasing Ni(II) concentration.

The experimental data was utilized for the simulation of BOD exertion in the presence of various Ni(II) concentration and the BOD exertion model proposed by Swamee and Ojha was found to be satisfactory. A commonly used modelling approach, Thomas method,was also applied to the data; however, the results are unsatisfactory in the presence of Ni(II).

Experimental results indicated that, Ni(II) is toxic to BOD and the degree of toxicity depends on the level of Ni(II) in the wastewater.

Key Words: BOD, modelling, effect of Ni(II), BOD parameters, heavy metals, BOD exertion curve

Science Code: 615.02.01

ÖZ

Ni(II)'NİN BOİ ÜZERİNE ETKİLERİ-BOİ EĞRİSİ MODELLEMESİ

YÜCEL, Gamze

Yüksek Lisans Tezi, Çevre Bilimleri Ana Bilim Dalı

Tez Yöneticisi: Yrd. Doç. Dr. Ülkü YETİŞ

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Bu çalışmada, Ni(II) nin BOİ üzerindeki toksik etkileri araştırılmış, Ni(II) içeren atıksularda BOİ'nin değişimi gözlenmiştir.

Bu amaçla, değişik Ni(II) konsantrasyonlarını (1.0, 2.0, 3.0, 4.0, 5.0 ve 10.0 mg/L) içeren sentetik atıksuyun 20 gün süresince BOİ değerleri ölçülmüş, yapılan literatür araştırmalarından da beklendiği üzere, artan Ni(II) konsantrasyonu ile birlikte BOİ değerlerinde azalma gözlenmiştir.

Ayrıca, deneyler sonucunda elde edilen veriler değişik Ni(II) konsantrasyonlarında, BOD eğrisi modelleme çalışmaları amacıyla kullanılmış ve Swamee ve Ojha modeli ile beklenilen sonuçlar alınırken, kullanımı yaygın bir model olan Thomas metodu ile beklenilen sonuçlar alınamamıştır.

Anahtar Sözcükler: BOİ, modelleme, Ni(II) nin etkisi, BOİ parametreleri, ağır metaller, BOİ eğrisi

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NOMENCLATURE

k	reaction rate constant(according to base e), day^{-1}
k''	reaction rate constant(according to base 10), day^{-1}
t	time, day
L	ultimate BOD, mg/L
L_t	amount of the first stage BOD remaining in the water at time t, mg/L
y	amount of BOD exerted at time t, mg/L
y_c	BOD exerted at time t_c, mg/L
y_o	constant related to the size of inocula and the microbial activities in the system
a	total carbonaceous BOD, mg/L
b	initial DO concentration, mg/L
n	order of reaction
m_c	rate exponent for carbonaceous stage
t_c	apparent time of reaching the first stage BOD, day
n_t	transition exponent
m_L	slope of the BOD exertion curve
$w_p L$	plateau BOD, mg/L
m_{ca}	slope of the BOD exertion curve prior to occurence of plateau
t_p	time at which plateau starts, h_{-1}
t_{cL}	time at the end of plateau, h_{-1}
m_{cL}	rate exponent
m_{cb}	rate exponent

S = S(t) stationary random process accounting for the noise in the process

CHAPTER I

INTRODUCTION

The biochemical oxygen demand (BOD) is usually defined as the amount of oxygen utilized by bacteria during the oxidation of organic material contained in a wastewater sample (Benefield and Randall, 1980). This test is based on the premise that all the biodegredable organic material contained in the in the wastewater sample will be oxidized to CO_2 and H_2O, using molecular oxygen as the electron acceptor. Therefore, it is a direct measure of oxygen requirement and an indirect measure of pollution biodegredable organic matter.

As various investigators reported, BOD test is widely used to determine the pollutional strength of domestic and industrial wastes in terms of the oxygen that they will require if discharged into natural watercourses in which aerobic conditions exist (Sawyer and McCarty, 1985; Tchobanoglous, 1981; Gaudy and Gaudy, 1980).

BOD data have wide application in environmental engineering practice. It is an important criterion used in water pollution control where organic loading must be restricted to maintain desired dissolved oxygen levels. The determination is used in studies to measure the purification capacity of receiving waters and serves regulatory authorities as a means of checking on the quality of effluents.

BOD is also a parameter of great importance in the design and operation of biological wastewater treatment processes. It is a factor in the choice of treatment method and is used to determine thesize of certain units, particularly trickling filters and activated sludge units. After treatment plants are placedin operation, the BOD test is used to evaluate the efficiency of various units. However, with the BOD test, only the biodegredable organics are measured and the test does not have stochiometric validity after the soluble organic matter present in the solution has been used.

As mentioned by Tchobanoglous(1981) despite the wide spread use of the BOD test, it has a number of limitations. Since this is a bioassay procedure, it is extremely important that environmental conditions be suitable for the living organisms to function in an unhindered manner at all times (Sawyer and McCarty, 1985). For example, the use of nonacclimated biological seed is probably the most common factor responsible for erroneous BOD results. Acclimated seeds can be developed in the laboratory by feeding the wastewater to be tested to an aerated flask of settled sewage organisms over a period of time. If the waste has been discharged to a stream for a considerable period of time, a water sample from the stream some distance below the outfall will usually contain a population of acclimated organisms. Settled effluent from a plant treating the some wastewater can also be used.

As another disadvantage of the BOD test; theoratically an infinite amount of time is required for the complete biological oxidation of the organic matter. But, for all practical purposes, the reaction may be considered complete in 20 days.

However, 20 day period is too long to wait for results, in most instances it has been found by experience that, a large percentage of total BOD is exerted in 5 days; consequently the test has been developed on the basis of a 5 days incubation period.

In fact, the BOD test may run the risk of not reflecting the true organic strength of the influent in the presence of inhibitors such as heavy metals and toxic organics (Artan and Orhon,1985). These metals which typically include nickel, chromium, copper, mercury, cadmium and zinc are placed among toxic materials that are presently receiving considerable attention in the environmental engineering literature (Yetiş, 1988).

Although it is associated with such risks or disadvantages, BOD is likely to remain in the future as an important water quality indicator (Leduc et al., 1985).

In this work, the effects of Ni(II) as an inhibitor on BOD exertion curve will be evaluated and modelling of the BOD curve in the presence of Ni(II) will be studied. It is known that, most of the models used to describe the laboratory BOD progression curve are of the deterministic type. The conventional method, Thomas method is generally used for evaluation of BOD parameters, k and L. As another approach, to describe the entire exertion process, Swamee and Ojha(1991) proposed a generalized BOD exertion equation valid over all the phases.

In this study, the comparison of applicability of both Thomas method and a model proposed by Swamee and Ojha in the presence of Ni(II) will be examined.

CHAPTER II

LITERATURE REVIEW

In this chapter, previous studies carried out until present that has been done on the kinetics of BOD exertion and modelling of the exertion curve will be reviewed. The effects of heavy metals on BOD kinetics especially Ni(II) will be emphasized.

2.1. BOD Progression Curve

As mentioned, BOD is the amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic conditions(Sawyer and McCarty, 1985). Since BOD reaction is closely related to a first order type of reaction, a plot of the amount of organic matter remaining versus time yields a parabolic curve. Likewise, if a plot is made showing the amount of organic matter oxidized versus time, another parabolic curve is obtained. Because oxygen is used in direct ratio to the amount of organic matter oxidized in biochemical oxidations, a plot of oxygen used versus time should produce a parabolic type of curve also. A typical BOD curve has same characteristics similar to those for the curve for organic matter oxidized during the first 8-10 days. Following that, the BOD curve decreases radically from the course. It would be expected to follow as a unimolecular or first order reaction.

A typical BOD progression curve was divided into five zones for discussion by Benefield and Randall (1980). These zones are illustrated in Figure 2.1.

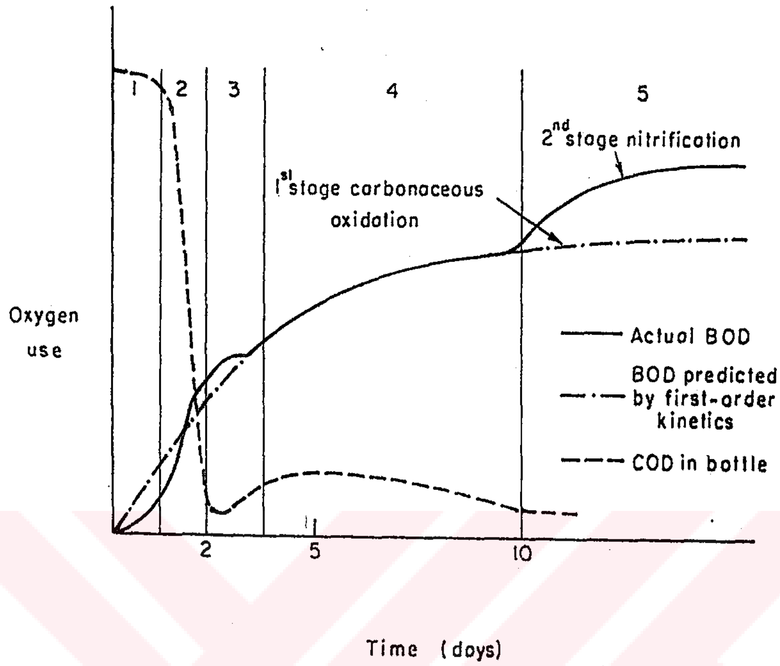


Figure 2.1.BOD Progression Curve

During the first stage; the lag and synthesis dip is due to a combination of retarded oxidation as the organisms acclimate to the substrate and reduced oxygen utilization during the high-synthesis phase. It should be noted that the BOD bottle becomes cloudy on the second day, indicating a large increase in microbial mass. Synthesis requires much less oxygen per unit of substrate utilized than does oxidation to carbondioxide. Synthesis and oxidation are given as:

Synthesis: $C_5H_{12} + 2.25\ O_2 \longrightarrow C_5H_7NO_2 + 2.5\ H_2O$

Oxidation: $C_5H_{12} + 8\ O_2 \longrightarrow 5\ CO_2 + 6\ H_2O$

The second stage; as the mass of microorganisms became large,the rate of synthesis decreases and the rate of oxygen reaction increases. This causes a very rapid oxygen utilization in this phase. At the end of second phase, as substrate becomes limiting, the rate of oxidation decreases. Reduced oxidation rates at the end of this phase may also be due to the fact that the more easily utilized materials have been assimilated and only the more difficult materials remain.

In the third phase; during the second or third day the microorganism concentration reaches a maximum and an oxidation plateau is reached. The reason for the plateau or third phase is not completely understood but it has been speculated that it is either due to changeover from external substrate to cellular materials as a food source with a slight acclimation period; or to the onset of rapid growth of predator organisms.

Fourth phase; the endogenous phase occurs after the plateau where cellular components are oxidized to provide energy for life-support functions.

During the fifth phase; at about 10 days, organisms that oxidize nitrogen compounds begin to predominate. The nitrifying organisms are probably present throughout the test, but because proteins are resistant to breakdown and much of the nitrogen is tied up in the protein, the nitrifiers do not predominate until nearly the end of the carbonaceous oxidation. This causes a second hump in the curve called the "second-stage BOD" or "nitrification".

2.2. Kinetics of BOD Reactions

2.2.1. First Order Kinetics of BOD Reactions

The oxygen utilization in the BOD test is a biological reaction. For this reason, the bacterial environmental conditions, the initial mass of organisms, acclimation of the bacteria to the organics, and the food/microorgaisms ratio are important variables and possible sources of differences in results (Benefield and Randall, 1980). Biochemical reactions usually involve a complex series of intermediate reactions, and it is impossible to provide an exact mathematically based, theoratical explanation for the oxidation. This is also valid for the BOD test. Nevertheless, it is generally assumed that BOD removal approximates first order kinetics; that is, the rate of BOD removal (rate of oxidation of organic matter) is directly propertional to the amount of BOD remaining at any time. Mathematically, the expression for the time progression is expressed as:

$$\frac{dL_t}{dt} = - k' L_t \qquad (2.1)$$

where;

t : time

L_t : amount of the first stage BOD remaining in the water at time t.

k' : reaction rate constant

This equation can be integrated as:

$$\ln L \Big|_0^t = -k' t$$

$$\frac{L_t}{L} = e^{-k't} = 10^{-kt} \qquad (2.2)$$

where;

L or BOD is the BOD remaining at time t=0 (ultimate BOD)

k" is the reaction rate constant.

The relation between k" and k is as follows:

$$k = \frac{k'}{2.303} \qquad (2.3)$$

The amount of BOD remaining at any time t;

$$L_t = L(10^{-kt}) \qquad (2.4)$$

and y, the amount of BOD that has been exerted at any time t.

$$y = L - L_t = L(1-10^{-kt}) \qquad (2.5)$$

This relationship is shown in Figure 2.2.

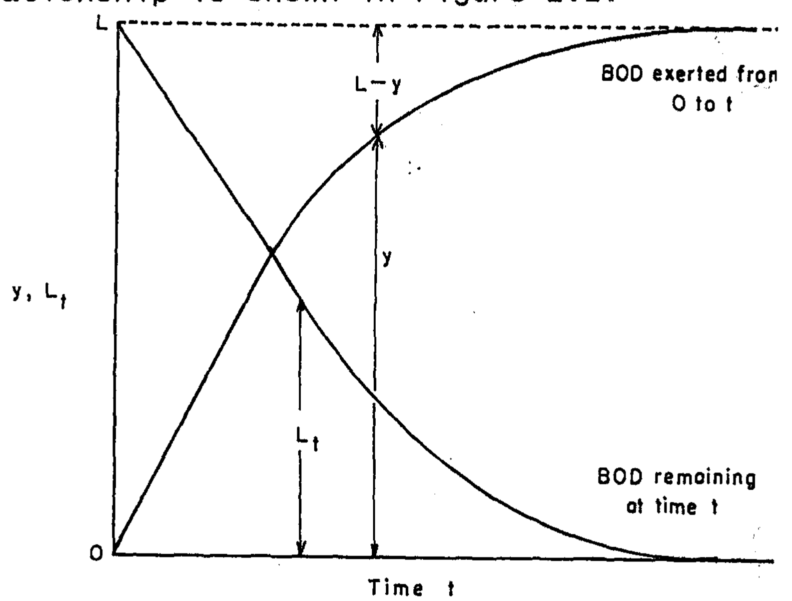


Figure 2.2. Formulation of the First Stage BOD Curve

2.2.2. Second Order Kinetics of BOD Reaction

One such alternative model that has received considerable attention is the second order model proposed by Woodward (1953). This model describes the rate of disapperance of organic matter as being proportional to the square of concentration of remaining organic matter, or

$$-\frac{dL}{dt} = kL^2 \qquad (2.6)$$

By integration and substitution of (L-y) for L gives:

$$y = \frac{L^2kt}{1+Lkt} \qquad (2.7)$$

where all the values are the same as those described in section 2.2 except the rate constant k which is in terms of $(mg/L)^{-1}.day^{-1}$.

2.2.3. Comparison of First and Second Order Kinetics

As various investigators (Streeter and Phelps, 1909; Theriault, 1927; Benefield and Randall, 1980; Metcalf and Eddy, 1979; Hewit at al., 1978) reported; in most cases, the BOD progression curve has been succesfully modeled using the first order kinetics. The first order model is extensively used by practising environmental engineers. Because it most often gives satisfactory results and mathematical formulation for first order kinetics is very simple. As it was strengthened by the studies of Berkün (1980), the first order relationship provides an acceptable model for the biological oxidation of complex substrates at least in the range of normal crude sewage samples.

Evaluation of the second order model has produced conflicting results. Certain investigators have found that the second order equation fits BOD data as well as the first order (Woodward, 1953; Young and Clark, 1965), or that it gives a better fit than the first order (Butts and Kothandaraman, 1970). Stones (1981) also confirmed that the rate of oxidation of carbonaceous matter in domestic sewage during the first stage was proportional to both its unsatisfied BOD and the residual DO concentration; and that the process therefore conformed to a second order kinetics.

$$\frac{dy}{dt} = k(a-y)\,(b-y) \qquad (2.8)$$

where;

a :total carbonaceous BOD

b :initial concentration of DO

Marske and Polkowski (1972) observed that, the second order model becomes more adequate as the first order reaction rate constant, k, value increases. This can be explained by the fact that as the first order k value increases, the resulting curve approaches a second order curve. It seems that when the first order k is in the region of 0.15 to 0.20 day^{-1} the data are described equally well by both models. However, when the first order k becomes greater than 0.20 day^{-1} the second order model describes the data more accurately than the first order model. This suggests that an estimator who uses a first order k of 0.20 day^{-1} or greater is underestimating the actual rate of the reaction. Therefore the use of the first order model should be limited to k values of 0.20 day^{-1} or less.

Hartmann and Wilderer (1969) studies on the differentiation of zero, first, second and third order of kinetics. They reported that, it is possible to describe the whole process by one mathematical formula. The process is composed of a set of single reactions, with each of them under the proper load values being the rate limiting one. At low load values, the second order reaction is the best approach.

2.2.4. A Multiorder Approach to BOD Kinetics

Such conflicting reports given in Section 2.2.3 suggest that, if the first and second order equations do not adequately describe BOD kinetics, then perhaps some other order kinetic equation could be superior to both (Hewitt et al.,1978).

If n is defined as the order of the reaction, then a generalized form of equation (2.1) would be:

$$-\frac{dL}{dt} = kL^n \qquad (2.9)$$

Upon integration and introduction of y this equation becomes

$$y = L-[(n-1)k+L^{(1-n)}]^{1/(1-n)} \qquad (2.10)$$

This equation is valid for any reaction order except the first where 1/(1-n) is meaningless.

The general trend observed is that, as n becomes larger, L also becomes larger. This is not a completely new observation, as other investigators (Young and Clark, 1965) observed that the second order L was approximately equal to 1.25 times the first order L. Hewit et al.,(1978) found out that, second order L values ranged from 1.23 to 1.25 times the first order values averaging 1.39, which is reasonably in a good agreement with the findings of Young and Clark (1965). According to the studies of Hewitt et al.,(1978) two approaches employed to observe which order might be considered convenient for BOD kinetics, whether from the standpoint of rate equations ability to closely fit the data points or its ability to predict later BOD values from early BOD measurements, 12 of 21 samples exhibited increasingly better performance as the order of the BOD equation increased from 1 to 4. Thus, although 5 samples best followed 1.5 order kinetics, two first order kinetics, and one each others 2.5 and 3, general trend was for better performance by the higher order equations.

Unfortunately, this trend towards better performance in both fitting data and predicting final BOD values from early measurements is achieved at least in part through increasingly larger calculated ultimate BOD values, so that as n proceeds from 1 to 4, the L values are more than doubled. Examination of the oxygen uptake curves suggests that these L values for higher ordered reactions are unrealistically high, and use of these equations to take advantage of their generally better performance must be weighed against the probability that the ultimate BOD values calculated from their use do not represent actual environmental levels.

2.3. Methods for the Estimation of BOD Parameters(k and L)

Benefield and Randall (1980) reported that, the rate at which organic materials oxidized is dependent upon several factors, such as temperature, nutrients, biological population etc., and it is reflected by magnitude of the reaction rate constant k. To obtain more complete information on the extent and the rate of decomposition, the constants L and k must be determined. The significance of k in determining cause of the BOD reaction is illustrated in Figure 2.3.

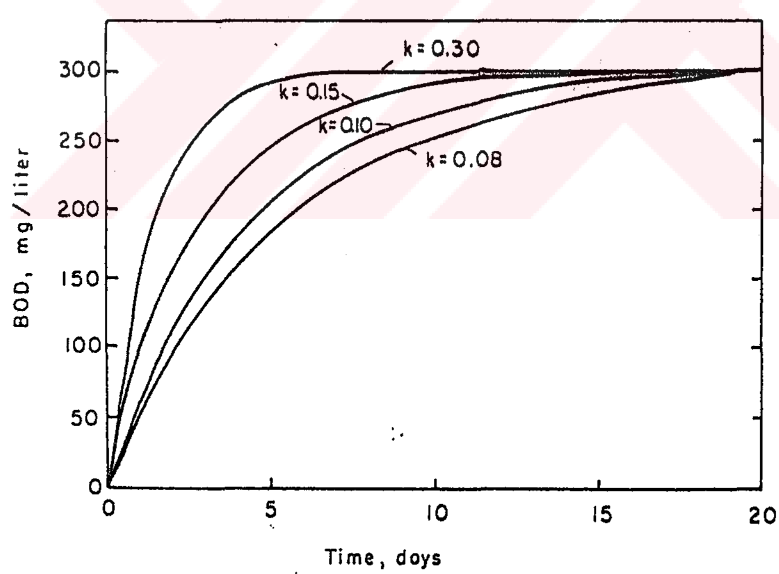


Figure 2.3.Effect of Reaction Rate Constant on BOD
(For a Given L Value)

The rate of biochemical reaction, or rate constant k, can be evaluated in a number of ways:

THE LEAST SQUARE METHOD: This method can be used for first and second order reactions.

$$\frac{dy}{dt} = k' (L-y) \qquad (2.11)$$

In this equation both k' and L are unknown. If it is assummed that, dy/dt represents the value of the slope of the curve to be fitted through all the data points for a given k' and L value, then because of experimental error, the two sides of Equation (2.11) will not be equal but will differ by an amount R. Rewriting Equation (2.11) in terms of R for the general case yields:

$$R = k'(L-y) - \frac{dy}{dt} \qquad (2.12)$$

Simplifying and using the notation y' for dy/dt gives

$$R = k'L - k'y - y' \qquad (2.13)$$

Substituting "a" for k'L and "-b" for k' gives

$$R = a + by - y' \qquad (2.14)$$

If the sum of the squares of the residuals R to be a minimum, the following equations must hold:

$$\frac{d\Sigma R^2}{da} = \Sigma 2R \frac{dR}{da} = 0$$

$$\frac{d\Sigma R^2}{db} = \Sigma 2R \frac{dR}{db} = 0 \qquad (2.15)$$

If the indicated operations in equation (2.15) are carried out using the value of the residual R defined by equation (2.14), the following set of equations result:

$$na + b\Sigma y - \Sigma y' = 0 \qquad (2.16)$$

$$a\Sigma y + b\Sigma y^2 - \Sigma yy' = 0 \qquad (2.17)$$

where;

n : number of data points

k' : -b(base e)

L : -a/b

THOMAS METHOD: This method is based on the similarity of two series functions.

$$\left(\frac{t}{y}\right)^{1/3} = (kL)^{-1/3} + \frac{k^{2/3}}{6L^{1/3}}\, t \qquad (2.18)$$

According to equation (2.18), when (t/y) versus t was plotted a line with a intercept of, $(kL)^{-1/3}$ and with a slope of $k^{2/3}/6L^{1/3}$ is obtained (Figure 2.4).

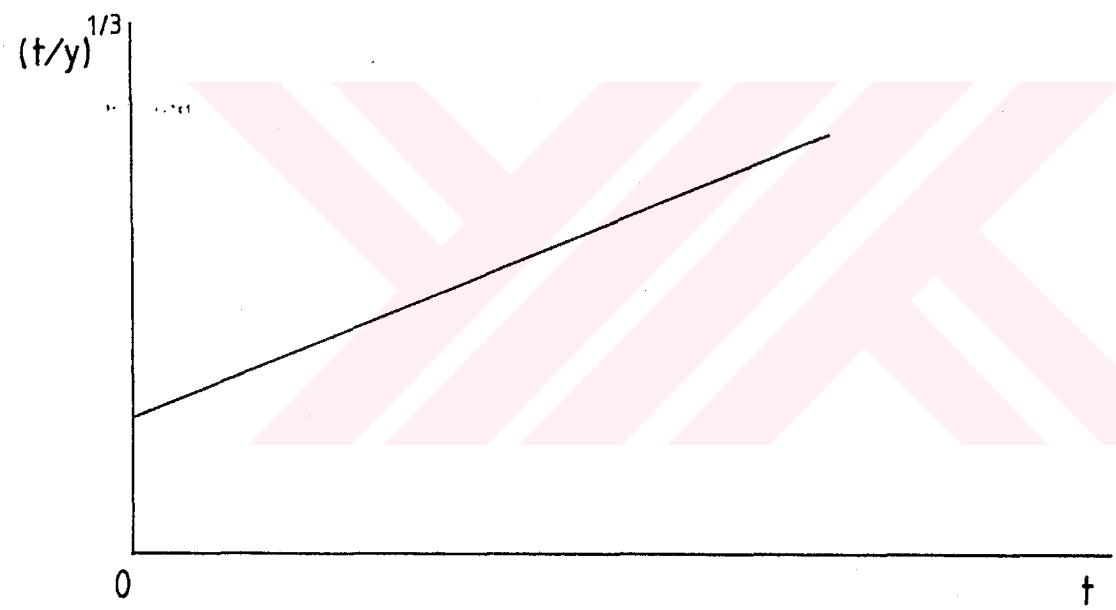


Figure 2.4. t versus $(t/y)^{1/3}$ Transformation of Data

MOMENTS METHOD: This method is based on taking moments of the determined values above the vertical coordinate axis of BOD versus time curve. A similar curve is computed which yields he value of L. These curves given in Figure 2.5 can be applied only to a specified time sequence of observation which must be selected in advance.These curves can only be used for 1, 2, 3, 14, 5, 6, 7 day BOD vaues or an exact multiple of these days.

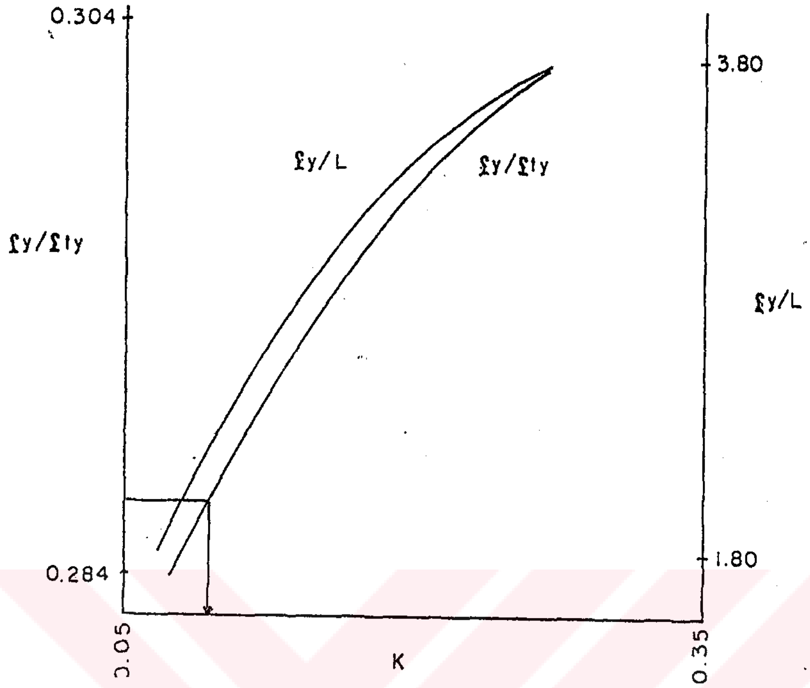


Figure 2.5. Moments Method Calculation Chart

SLOPE METHOD: This method assumes a linear relationship between the rate of BOD exertion and the BOD itself.

$$\frac{dy}{dt} = k(L-y) \quad (2.19)$$

By applying least square method;

$$R = k(L-y)-dy/dt \quad (2.20)$$

substituting for "a" for kL and (a - b) for k;

$$R = a+by-y'$$

$$\Sigma R^2 = \Sigma(a+by-y')^2$$

2 normal equations,

$$na+b\Sigma y-\Sigma y''= 0$$
$$a\Sigma y+b\Sigma y^2-\Sigma yy''= 0$$

n is the number of data.

$$y' = \frac{y_{n+1} - y_{n-1}}{t_{n+1} - t_{n-1}}$$

By solving above two normal equations k and L can be calculated.

Berkün (1974) compared the k values, calculated using the method of moments given by Moore et al. (1950), and the new equations given by the author which provide the convenience of calculating the k values directly from daily BOD data (See Appendix B). The results obtained from his studies have indicated that the method of moments is a reliable method, it gives better estimates than the other equations. Because a satisfactory linearship between first order parameters and obtained from methods of moments and second order parameters using crude sewage data.

Marske and Polkowski (1972) studied to obtain concrete evidence on the quality of the methods used to estimate k and L. They concluded that methods of moments of estimating the first order BOD parameters, k and L, is the best method when the estimator does not have access to a digital computer.The

Thomas Slope Method consistently underestimates the k constant and consiquently overestimates the ultimate BOD.

2.4. Effects of Heavy Metals on BOD

As it is known, one of the functions of BOD is to evaluate the efficiency of various treatment plants. On the other hand, many municipal treatment plants receive wastewaters containing heavy metals due to the increasing trend towards combining municipal and industrial wastes. These metals which include nickel, chromium, copper and zinc are placed among toxic materials that are presently receiving considerable attention in the environmental engineering literature.

Heavy metals are often in soluble form in wastewaters. The soluble forms of heavy metals are considered most toxic as toxicity and availability to biological systems increase with the increasing solubilities(Sujarittanonta and Sherrard, 1981). The general effect of heavy metals on biological reactions can be seen from Figure 2.5.

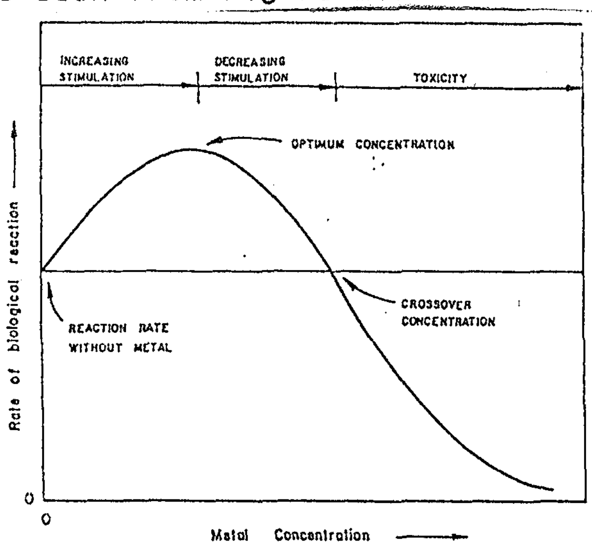


Figure 2.6. General Effects of Heavy Metals on Biological Reactions (McCarty, 1964)

At low concentrations of heavy metals, an increase in biological reaction rate is observed. That means, low concentrations of heavy metals stimulate the biological reactions. However, increased concentrations of the heavy metal cause in decrease in stimulation , and then a point is reached at which the stimulation disappears. Beyond this point, the rate of biological reaction is less than the no-metal condition case. Finally, at relatively high concentrations, bacterial activity approaches the zero.

As various investigators (McCarty, 1964; Bagby and Sherrard, 1981; Chang et al., 1986; Lamb and Tollefson, 1973; Kugelman and McCarty, 1964) reported, microorganisms usually have the ability to adapt some extent to inhibitory quantities of toxic materials during long term exposure. This adoptation is called acclimation and the extent of adoptation is changeable(McCarty, 1964). In some cases, the activity of microorganisms after acclimation may approach that obtained in the absence of toxic material; but in other cases it may not.

Although some researchers have investigated the effects of some inorganic metal compounds on BOD, no effort has been made to study the effect on the growth of bacteria comperatively. Baker (1971) showed that, even very small concentrations of $HgCl_2$ can effect the values using the standard dilution technique. Dawson and Jenkins (1959) studied the effects of Cu, Ni, Zn, Cd and Cr on BOD using Warburg apparatus.

Berkün (1980) studied the effects of inorganic metal toxicity on BOD. He found that, when inorganic chemicals were used in smaller concentrations, microorganisms acclimated themselves to the medium, and after initial lag, oxygen uptake started.- Higher BOD was observed when lower concentrations of metal compound was used. And these differences remained unchanged throughout the 5 days period. Berkün concluded that, treshold concentrations. the inorganic chemicals found different than the other researchers (Barth et al., 1965; Baker, 1971; Maloney et al., 1959; Dermott et al., 1963). These differences may be caused by one or more of the following factors:

1. Type of BOD measurement technique used
2. Composition of media
3. Characteristics of media
4. Species strain type and number of microorganisms in the seed.

Mowatt (1976) investigated the relation between heavy metal concentration and quality of suspended solids (SS) while dealing with the effects of heavy metals on BOD test and observed that the toxic concentration often seemed to be related to the quantity of SS. This is logical in view of the fact that in bacteria, one would expect that the toxicity of a given substance is a function of the biomass affected. It should be taken into account that metal ions not only affect the bacteria by inactivation of their enzyme systems or in other ways, but also can react with chemicals in solution and solids in suspension or be removed by simple adsorption on the solids thus lowering the effective concentration of the metals in solutions.

As Mowatt (1976) also reported, a more important limitation of the BOD method is that the essential minerals in the dilution water effect the solubilities of many metals, precipitating them out of solution to some extent and thereby reducing the actual amount of ionized metal present to produce toxic effects.

2.4.1. Effect of Ni(II) on BOD

A very limited number of studies have been done on the effect of Ni on BOD. As mentioned earlier, evaluation of plant performance with BOD experiments suffers a major drawback. For example, if one considers the toxicity of heavy metals to the microorganisms in the BOD bottle, then the observed readings will be sum of the effects on the BOD test itself and effects on the actual plant performance. Percent reductions observed in overall removal were 1 and 3 % for 5 and 10 mg/L of Ni(II) doses respectively. However their run with 2.5 mg/L Ni(II) was notable as the percent reduction achieved in this run was greater than the 5 and 10 mg/L runs. They observed a 5 % reduction in overall BOD removal efficiency for the 2.5 mg/L run. On the basis of these observations, they concluded that the maximum level of Ni which will not produce a detectable effect on treatment efficiency is greater than 1 mg/L and less than 2.5 mg/L. Mc Dermott et al. (1965), also concluded that hetero trophic organisms could tolerate without reduced efficiency a continuous dose of 1 mg/L. Thus a Ni concentration of 1 mg/L is the treshold limit. Contrary to the findings of Mc Dermott et al., (1965), Research Comittee (1950) reported that; concentration of 6 mg/L Ni has a treshold effect where 10 mg/L has a very pronounced effect.

Gökçay and Hatipoğlu (1984) showed that the measured BOD may increase with the increasing dilution in the BOD bottle, and the reason for this effect was speculated as the presence of toxic heavy metals in an effluent which was diluted in the BOD bottle with the accomponying lessening in their toxic effect or microorganisms.

Artan and Orhon (1985) studied the impact of inhibition on the BOD kinetics by selecting Ni and Cd as inhibitors and concluded that, BOD test may be used as an instrument to assess the impact of inhibitors on biochemical reactions. The effect of several factors such as nickel concentration, the organic content, the dilution rate may be evaluated using the standard test procedure. The mathematical interpretation of inhibitory actions is simplified when incorporated into BOD kinetics, due to low substrate concentrations. The approach may be used to define a constant, k, characterizing inhibition effects. In contrast to these findings, Yetiş (1988) found that, microorganisms will be adopted to Ni(II) if sufficient acclimatization period is allowed. The author studied the effects of Ni(II) on the completely mixed activated sludge process, at concentrations of 5.0, 10.0 and 25.0 mg/L respectively.

The variable effects of 5.0 mg/L Ni(II) on the performance of the activated sludge unit with the changing dilution rates was attributed to the heterogenous nature of the activated sludge. It was reasoned that, the selection imposed on the various species of organisms by the presence of Ni(II) or changing dilution rates may have led to the suppression or the overgrowth of certain species which in turn affected changes in the biokinetic constants of the system. It is also found that, Ni(II) concentration of 25.0 mg/L was completely toxic to the activated sludge process and that the treshold concentration of Ni(II) is higher than 10.0 mg/L. The fact that a continuous culture system could be maintained at this state remains unexplained. Thus, one can expect to have the microorganisms to be adapted to Ni(II) within the BOD bottle. If this is the case, than the BOD exerted at fifth day might be the actual second or third day BOD of that wastewater. That is to say that, the BOD exerted at certain day might correspond to the actual fifth day BOD exertion.

2.5. Modelling of the BOD Exertion Curve

As discussed in previous sections the BOD progression curve has been succesfully modelled using the first order kinetics. Most of these models which describe the laboratory BOD progression curve are of the deterministic type. However, BOD progression is not a simple process and it may not be possible to describe it adequately with deterministic models. According to Leduc et al., (1985) the process shows random fluctuations due to variability in the chemical and the biochemical composition of complex organic wastes and also due to the presence of heterogenous cultures of bacteria. Moreover, uncertainity in the measurements arising from instrumentation noise, sampling, analytical and data transmission techniques and errors are additive factors.

So, Leduc et al., (1985) developed a stochastic model as an alternative to deterministic models, that account for measurement of uncertainity and natural variability of the complex composition of the waste and the heterogenous biological populations involved. It is assumed that the process is driven by an input noise, this assumption being based on the fact that the BOD process is inherently subject to randomness and uncertainity.

Assuming that uncertainity appears in the form of in-additive random disturbance, then equation (2.22) can be written.

$$\frac{dL}{dt} = -kL + S \qquad (2.22)$$

where;

S = S(t) is a stationary random process accounting for the noise in the process.

Leduc et al., (1985) reported that, this model is generally applicable to any first order kinetics for BOD.

Maoyu (1990) proposed an autocatalitic model for the oxidation of carbonaceous matter. The effects of inoculum size and microbial activities on the kinetics of BOD where also taken into account by that model.

During the biochemical oxidation of carbonaceous organic matter, microorganisms play the role of catalyst, and by utilizing the energy evolved during the process, microorganisms continuously reproduce new ones which again catalyze the oxidation of organic matter. Therefore the biochemical oxidation of organic matter can be regarded as an autocatalytic reaction.

Maoyu (1990) assumed that the number of microorganisms reproduced is proportional to the amount of organic matter oxidized, in addition, is proportional to both its unsatisfied BOD and the residual concentration of DO and proposed an autocatalytic kinetics model:

$$\frac{dy}{dt} = k_3(a-y)(b-y)(y+y_o) \qquad (2.23)$$

where;

a : total carbonaceous BOD

y : BOD satisfied after time t

b : initial concentration of DO

y_o : constant related to the size of inocula and the microbial activities in the system

k_1, k_2, k_3 : velocity coefficients

This equation means that, the rate of oxidation of carbonaceous matter is proportional to its unsatisfied BOD, the residual concentration of DO and the quantity of microorganisms with given activities, which equals the addition of the quantity of the inocula (y_o) and the reproduced quantity (y).

Maoyu (1990) concluded that; the autocatalytic kinetic model can satisfactorily explain the problem of lag period in BOD test. If the size of inocula and/or the microbial activities increase adequately so that y_o is large enough to make $(b-y)(y+y_o)$ become constant, the autocatalytic kinetics model can be expressed as first order kinetics and if the size of the inocula and/or microbial activities increase greatly so that y_o is very large as compared with a autocatalytic kinetics can be converted into second order kinetics.

Since the BOD kinetics models describe a particular phase or stage only, and lack in general applicability over the entire exertion process, Swamee and Ojha (1991) proposed a generalized BOD exertion equation valid over all the phases.

During the carbonaceous phase for an acclimated seed with moderate temperature substrate, the BOD exertion starts initially, showing an increasing rate kinetics for a very short duration(perhaps in hours). For such a case the BOD curve can be modelled as;

$$y=L[(t_c/t)^{m_c/n}+1]^{-n} \qquad (2.24)$$

where;

m_c :exponent for the carbonecaous stage

t_c :apperant time of reaching the first stage BOD

n :transition exponent given by;

$$n = -1.4427 \ln y_c/L$$

y_c :BOD exerted at time t_c

Thus all the parameters of equation (2.24) can be evaluated, if BOD exertion data are available for a sufficiently long time. He reported that, during the lag phase, equation (2.24) can be expanded as;

$$y=L[(t_L/t)^{m_l/n} + (t_c/t)^{m_c/n} + 1] \ldots\ldots\ldots (2.25)$$

where m_L is the slope of the BOD exertion curve (on double logarithmic plot) for the time $t<t_L$ (lag time).

The equation for two stage BOD exertion curve with a plateau in the carbonaceous stage is given as:

$$y = w_p L \left[(t_p/t_L)^{m_{ca}/n}(t_L/t)^{m_L/n} + (t_p/t)^{m_{ca}/n} + 1\right]^{-n} +$$

$$(1-w_p)L\left[(t_c/t_{cL})^{m_{cb}/n}(t_{cL}/t)^{m_{cL}/n} + (t_c/t)^{m_{cb}/n} + 1\right]^{-n}$$

$$+ (w_n-1)L * \left[(t_n/t_s)^{m_n/n}(t_s/t)^{m_s/n} + (t_n/t)^{m_n/n} + 1\right]^{-n} \qquad (2.26)$$

where;

$w_p L$: the plateau BOD

m_{ca} : the slope of BOD exertion curve prior to the occurance of plateau

t_p : the time at which the plateau starts

t_{c1} : the time of the end of the plateau

m_{c1} : the corresponding exponent

m_{cb} : the slope of the BOD curve

As mentioned before, a generalized BOD equation proposed that model involving the log phase, plateau and the second stage can be converted to special forms with the exceptions of particular phases or stages.

CHAPTER III

SCOPE AND PURPOSE

As reviewed, the BOD test may run the risk of not reflecting the true organic strength of the influent in the presence of heavy metals. However, acclimitization might take place during the exertion. If this is the case, then it might be possible to predict the actual BOD_5 value for the wastewater containing heavy metals at relatively low concentrations.

Thus, the purpose is to investigate the effects of Ni(II) and to model BOD exertion in the presence of Ni(II).

To this purpose, two sets of experiments were conducted by adding 1.0, 2.0, 3.0, 4.0, 5.0 and 10.0 mg/L Ni(II) to the synthetic wastewater and BOD exertions were measured daily for a period of 20 days. The experimental data obtained was utilized for the simulation of BOD exertion in the presence of various Ni(II) concentrations. A commonly used deterministic model, namely, Thomas method and a model proposed by Swamee and Ojha (1991) were applied to investigate the effects of Ni(II) on BOD exertion and on BOD parameters, k and L.

CHAPTER IV

MATERIALS AND METHODS

To assess the effect of Ni(II) on BOD kinetics, 20 days BOD experiments were conducted. To ascertain the effect of different Ni(II) concentrations, two series of tests were carried out by adding 1.0, 2.0, 3.0, 4.0, 5.0 and 10.0, mg/L, of Ni(II) to synthetic wastewater. The method given in "Standart Methods for the Examination of Water and Wastewater" (See Appendix A) was applied for BOD determination. Experiments were carried out with a synthetic wastewater with the contituents given in Table 4.1. During the experiments, all the variables were kept constant except for Ni(II) concentrations.

4.1. Materials Used

4.1.1. Preperation of Synthetic Wastewater

Throughout the experiments, synthetic wastewater with known metal concentrations were used as wastewater sample. The basic constituents and the concentrations in the wastewater are shown in Table 4.1.

Table 4.1. Composition of Synthetic Wastewater

Constituents	Concentration(mg/L)
Proteose pepton	55.94
NaCl	18.65
Na_2SO_4	44.60
K_2HPO_4	44.60
$MgCl_2.6H_2O$	3.70
$FeCl_2.2H_2O$	3.70
$CaCl_2.2H_2O$	3.70
$MnSO_4$	$57x10^{-3}$
H_2MoO_4	$31x10^{-3}$
NaOH	$8x10^{-3}$
$ZnSO_4$	$46x10^{-3}$
$CoSO_4$	$49x10^{-3}$
$CuSO_4$	$76x10^{-3}$

Proteose pepton (Oxoid) was the sole source of organic carbon and organic nitrogen. The concentration of the pepton in the synthetic medium was adjusted as 55.94 mg/L. This pepton concentration corresponded to a protein concentration of 29.76 mg/L. Such a low organic content was delibaretly adjusted in order to minimize the dilution in BOD. Phosphate salts were added to the medium to provide phosphorus as well as to maintain pH stable at 7.0. The quantities of nitrogen and phosphorus were adjusted to allow carbon growth limiting. All the other nutrients were added in sufficient quantities to satisfy the growth requirements of the bacteria.

In preparing synthetic wastewater, firstly, 0.3 g of proteose pepton and 0.1 g of NaCl were dissolved in 500 ml of distilled water to prepare pepton solution, then, Solution A, B, C were prepared according to compositions given below:

SOLUTION A:

$MnSO_4.H_2O$	68.83 mg/L
MoO_3	30.00 mg/L
NaOH(0.05N)	8.35 mg/L
$ZnSO_4.6H_2O$	37.89 mg/L
$CaCl_2.6H_2O$	80.78 mg/L
$CuSO_4.5H_2O$	81.70 mg/L

SOLUTION B:

KH_2PO_4	$25x10^3$ mg/L
Na_2SO_4	$25x10^3$ mg/L

SOLUTION C:

$MgCl_2.6H_2O$	10x10 mg/L
$FeCl_2.4H_2O$	$12.21x10^3$ mg/L
$CaCl_2.2H_2O$	$10x10^2$ mg/L

Having the proteose pepton solution, and solutions A, B and C in hand, synthetic wastewater was prepared by adding 300 ml of proteose pepton solution, 3,25 ml of 6.25 ml of Solution B and 1.3 ml of Solution C to 3217.5 ml of tap water. The resulting composition of the synthetic wastewater is given in Table 4.1.

4.1.2. Preperation of Nickel Stock Solution

Nickel stock solution with a concentration of 10 g/L was prepared by utilizing the salt of $NiCl_2H_2O$. The desired concentration of Ni(II) was maintained by adding required amount of Ni(II) stock solution into synthetic medium.

4.1.3. Dilution Water

A wide variety of waters have been used for BOD work. Thorough long experience it has developed that; a synthetic dilution water prepared from distilled or demineralized water is best for BOD testing, because most of the variables like microorganism population, mineral content etc. can be kept under control (Sawyer and McCarty, 1985). Thus throughout this study, distilled water saturated with oxygen was utilized. Aeration was supplied for two days to ensure that the distilled water is saturated with oxygen.

In Winkler BOD determination, it is essential to have suitably diluted samples so that adequate nutrients and oxygen will be available during the incubation period (Tchobanoglous, 1981).

In the literature, it is advised to set three different dilutions. However, when the strength of a waste is known with some assurance two dilutions may be sufficient. Hence, throughout this study, in the first set of experiments two dilution ratios, namely, 1/25 and 1/50 dilotion were applied. Since satisfactory results were obtained from the lower dilution ratio, 1/25 dilution ratio was applied in this study.

4.2. Seeding

The dilution water should always be "seeded" with wastewater or other material to ensure an uniform population of organism in various dilutions and to provide an opportunity for any organic matter present in the dilution water blanks to be exposed to the same type of organisms as those in the wastewater.

Experience has shown that, domestic wastewater provides about as well balanced a population of mixed organisms as anything, and usually 2 ml of wastewater per liter of dilution water is sufficient. In this study, settled domestic sewage obtained from Middle East Technical University Treatment plant entrance has been utilized. t Sewage samples were stored at 20°C for 36 hours and 2 ml of this wastewater was added to each liter of dilution water.

The dilution water containing the seeding material will contain organic matter and that addition of the diluting water to the sample will increase the amount of oxidizable organic matter, therefore, a correction must be applied. This is achieved by using blank values. Blanks serve as the reference value from which all calculations of BOD are made. To have statistical reliability two blanks were analyzed for each concentration of Ni(II).

Thorough, the experiments BOD bottles were equipped with water seal to prevent entering of air during the incubation period and they are cleaned to be free of organic matter. This cleaning is accomplished by two rinses with tap water and a final rinse with distilled water.

Finally, blanks and the diluted samples were incubated for 20 days in the dark at 20 C. DO values of incubated samples and the blanks were determined using the azide modification of the iodometric method. (See Appendix A).

4.3. Calculation of BOD

$$BOD\ (mg/L) = (DO_b - DO_i)\ \frac{\text{Volume of the bottle}}{\text{Volume of the sample}}$$

where:

DO_b : Dissolved oxygen value found in the blank,mg/L

DO_i : Dissolved oxygen value found in the diluted samples,mg/L

CHAPTER V

RESULTS AND DISCUSSION

5.1. Experimental Results

In order to examine the BOD exertion curve under the effect of heavy metals, laboratory BOD bottle test have been performed. Ni(II) was selected as the toxicant or heavy metal and standard 2 days BOD experiments were run for various concentrations of Ni(II).

Varying amounts of Ni(II), namely, 1.0, 2.0, 3.0, 4.0, 5.0 and 10.0 mg/L were added to the synthetic wastewater and two different sets of experiments were conducted with this wastewater.

To obtain baseline data, BOD of synthetic wastewater without nickel was also determined for each set of experiment.

In order to decide on the dilution ratio to be employed in BOD tests, initially two different ratios, namely, 1/50 and 1/25 were tried. The results revealed that, the dilution rate of 1/25 is enough for getting BOD readings and there is no need for higher dilutions rates.

5.1.1. First Sets of Experiments

In the first set of experiments, BOD values for the Ni(II) concentrations of 1.0, 2.0, 3.0, 4.0, 5.0 and 10.0 mg/L were determined daily for a period of 20 days. The results obtained from this study are presented in Table 5.1 (See also Appendix C), and the percent effects of Ni(II) on the exerted BOD are tabulated in Table 5.2. The values presented in this table are the arithmetic averages of the measurements obtained from parallel experiments.

Table 5.1. Effect of Ni(II) (mg/L) on BOD Exertion

Days	0.0	1.0	2.0	3.0	4.0	5.0	10.0
0	0	0	0	1.25	0	0	0
1	5	2.50	2.50	0	0	0	0
2	5	2.50	7.50	0	2.50	0	0
3	5	5	12.50	6.25	5	21.25	15
4	10	5	15	6.25		11.75	7.50
5	10	6.25	7.50	7.50	5	10	10
6	12.50	2.50	7.50	18.75	2.50	11.75	8.75
7	12.50	10	15	7.50	7.50	16.25	12.50
8	10	5	16	5	7.50		
9	12.50	5	14.75	2.50	10	5	5
10	15	10	20.13	3.75	15	11.25	13.75
11			22.5	11.25		15	11.25
12	10	7.50	22.5	18.75	0	17.50	12.50
13	35*	7.50			5	15	12.50
14				11.25		17.50	15
15	10	8.75		7.50	7.50	18.75	15
16	47.50*	7.50		7.50	5	18.75	12.50
17		5	15.05	13.75	7.50	20	15
18			24.93	13.75		18.75	15
19		12.50		10	7.50	11.25	12.50
20	20	15	21.25	11.25	7.50	20	17.50

* : Due to the experimental errors (Bubbles were seen during the observations)

Table 5.2. Effect of Ni(II) on Mean BOD Values(mg/L)

Days	Percent Effect of Ni(II) on BOD Exertion					
0.0	1.0	2.0	3.0	4.0	5.0	10.0
1	50	50	100	100	100	100
2	50	150	100	50	100	100
3	0	250	125	0	425	300
4	50	300	37.5	-	112.5	25
5	37.5	25	25	50	0	0
6	80	40	150	80	10	30
7	20	120	40	40	130	0
8	50	160	50	25	nda*	nda*
9	60	164	80	20	60	60
10	33	134	75	0	25	8
12	25	225	-	100	175	125
13	79	nda*	nda*	86	57	64
15	12.5	nda*	nda*	25	187	0
16	84	nda*	76	89	61	74
20	25	225	44	62.5	0	13

* : no data available

As it can be seen from Table 5.2, addition of 2.0 mg/L Ni(II) to the synthetic wastewater caused an increase in BOD exertion for all the days except first, fifth and sixth days. At this Ni(II) concentration, BOD_{20} of the wastewater increased to 21.25 mg/L, although it was 20 mg/L in the absence of Ni(II). However, the difference between these two values are not so high and they can be easily accepted as equal.

According to the findings of Berkün (1980), as heavy metal concentration is increased, BOD exertion will be decreased; or higher BOD values would be observed in the absence of heavy metals. Similarly, Morgan and Lackey (1958) also reported that, the heavy metal toxicity is usually evidenced by an increase in BOD with increasing dilution. Parallel to these findings, in this set of data, although a gradual decrease in BOD with gradual increase in Ni(II) concentration was not observed, there was a decreasing trend in BOD exertion in the presence of Ni(II) with the exception of 2.0 mg/L Ni(II). At this Ni(II) concentration (Figure 5.12) ultimate BOD exertion was much higher than those of other concentrations. On the other side, the addition of 5.0 mg/L Ni(II) into the synthetic medium did not cause any change on BOD_{20} and the addition of 10.0 mg/L Ni(II) caused a slight decrease in BOD_{20}. The BOD_{20} in the presence of 10 mg/L Ni(II) decreased to 17.5 mg/L from the earlier 20 mg/L. Another observation was that addition of 1.0, 3.0 and 4.0 mg/L Ni(II) concentrations decreased the BOD_{20} exertion gradually, as was expected (Table 5.1).

Since the results obtained from this set of experiments were somehow cotradictory, it was essential to repeat the experiments and to prove the validity of the data obtained. To this purpose, a second set of experiments were run for the same Ni(II) concentrations and great care was taken for holding all environmental parameters constant. To minimize the experimental errors, synthetic wastewater to be utilized in second set of experiment prepared as a large batch and this batch of wastewater was utilized for all the BOD bottles by simply varying the quantity of Ni(II) in the bottles.

5.1.2. Second Set of Experiments

In this set of experiments, since it was aimed to use the same batch of synthetic wastewater and to obtain data for all Ni(II) concentrations at once, it was impossible to measure BOD exertion for all the days; thus, only fifth and twentieth day BOD exertions were measured. The whole data obtained from this set of experiments are given in Table 5.3 as a summary (See also Appendix D) and the percent effect of Ni(II) on BOD exertion is presented in Table 5.4.

Table 5.3. Effect of Ni(II)(mg/L) on BOD Exertion

Days	0.0	1.0	2.0	3.0	4.0	5.0	10.0
0	0	2.5	2.5	0	0	0	0
5	38.3	25	25	20	15	21.25	22.5
20	97.5	22.5	27.5	32.5	22.5	17.5	17.5

Table 5.4. Effect of Ni(II) on Mean BOD Exertion

Days	Percent Effect of Ni(II) on BOD Exertion					
	1.0	2.0	3.0	4.0	5.0	10.0
0	0	0	0	0	0	0
5	35	35	48	61	45	42
20	77	72	67	77	82	82

As it was expected, in these experiments, a gradual decrease in the measured BOD_5 and BOD_{20} was observed, when Ni(II) concentration was increased from 0.0 mg/L to 10.0 mg/L.

As can be seen from Table 5.4 that, even the highest concentration of Ni(II) applied in this set of experiment, namely, 10.0 mg/L did not completely inhibit the oxygen uptake but caused delay in BOD. The supression of BOD_{20} with 10.0 mg/L Ni(II) was about 82 % whereas the supression was about 42% for fifth day BOD. Similarly, for the lowest concentration tested, the percentage effect of Ni(II) on fifth day BOD was about 35 %, whereas it is about 77 % for twentieth day BOD. Thus, it is not wrong to generalize that the fifth day BOD exertion is about 50 % of the twentieth day BOD exertion for all the Ni(II) concentrations tested (Table 5.4). This observation might be speculated as the validity of the same rate expression for all Ni(II) concentrations.

Along this study, for the evaluation and discussion of experimental results, a combination of data from these two sets of experiments were used. To obtain more reliable and reproducable results, some of the extreme data points were not considered in this data evaluation. The resulting data set which will be used in modelling studies are presented in Appendix E. Table 5.5 is a summary table which tabulates the refined data from Appendix E.

Table 5.5. Effect of Ni(II) on BOD_5, BOD_{10} and BOD_{20}

Ni(II)(mg/L) conc.	BOD_5	BOD_{10}	BOD_{20}
0.0	10	15	50
1.0	5	10	15
2.0	7.5	20	25
3.0	20	12.5*	36
4.0	5	15	22.5
5.0	10	12.5	20
10.0	10	13.75	17.5

* : Eleventh day measurement

As it is seen from this table, BOD_5 and BOD_{10} were not seriously effected by the presence of Ni(II). There was only slight decreases in BOD_5 and BOD_{10} with an increase in Ni(II) concentrations. On the other hand, the net effects of these Ni(II) concentrations on BOD_{20} were considerable (Figure 5.1 5.3). For example, the same BOD_5 values obtained with no-nickel case and wastewater containing 5.0 and 10.0 mg/L Ni(II) concentrations (See Figure 5.1). During the examination of BOD_{10} values also, higher BOD value in the presence of 1.0 mg/L (13.75 mg/L) was observed compared to 1.0 mg/L Ni(II) concentration which has BOD_{10} reading of 10.0 mg/L (See Figure 5.2).

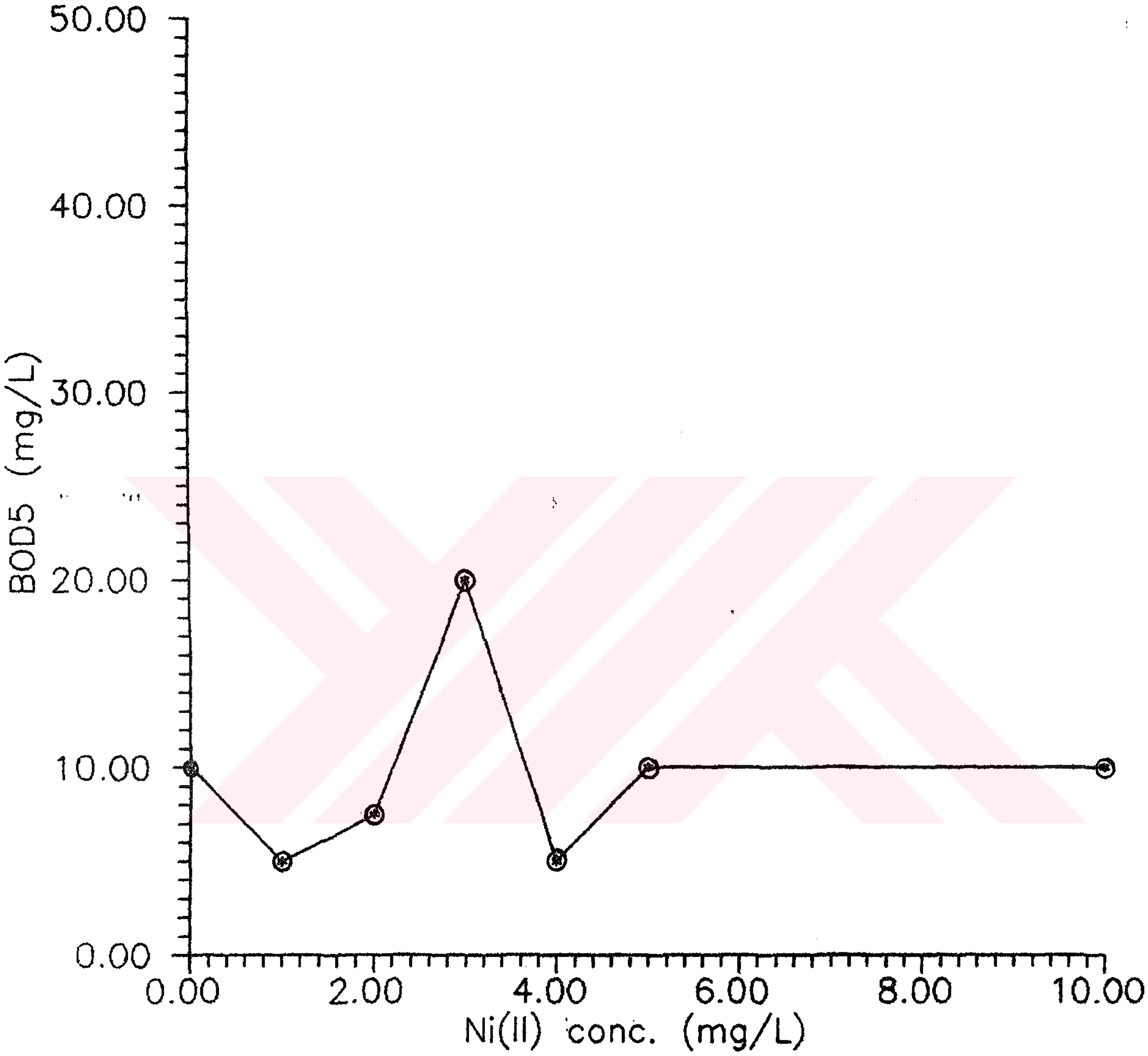


Figure 5.1. Effects of Ni(II) on BOD_5

However, Figure 5.3 shows that, there is a gradual decrease of BOD values with the increasing Ni(II) concentrations, with the exceptions of 1.0 and 3.0 mg/L Ni(II) concentrations.

This means, if the inconsistency of the BOD_{20} values measured by the addition of 1.0 and 3.0 mg/L Ni(II) is attributed to the experimental errors and inconsistent nature of the BOD experiment, other results obtained for ultimate BOD are as expected and confirmed by the studies of Berkün (1980).

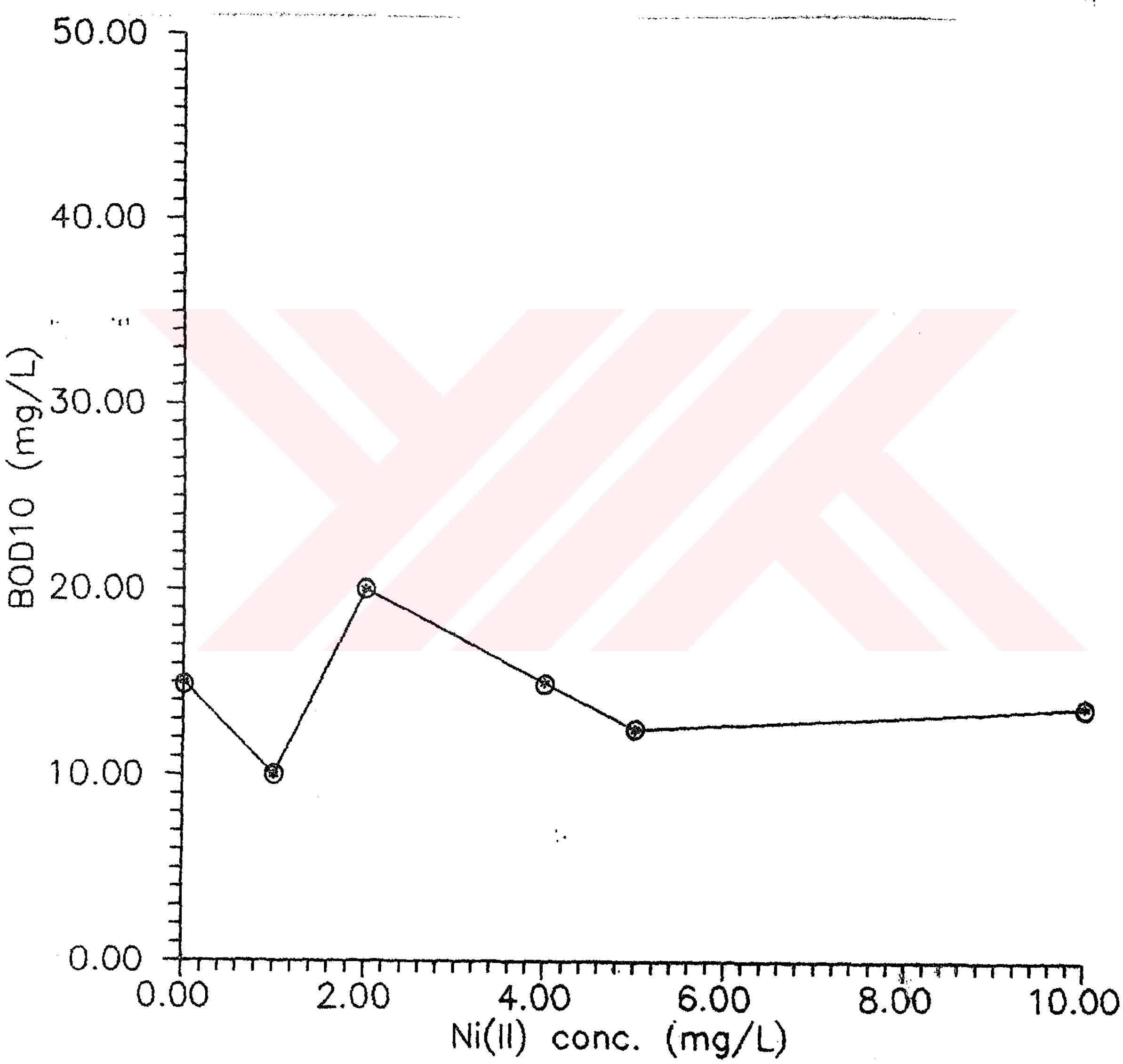


Figure 5.2. Effects of Ni(II) on BOD_{10}

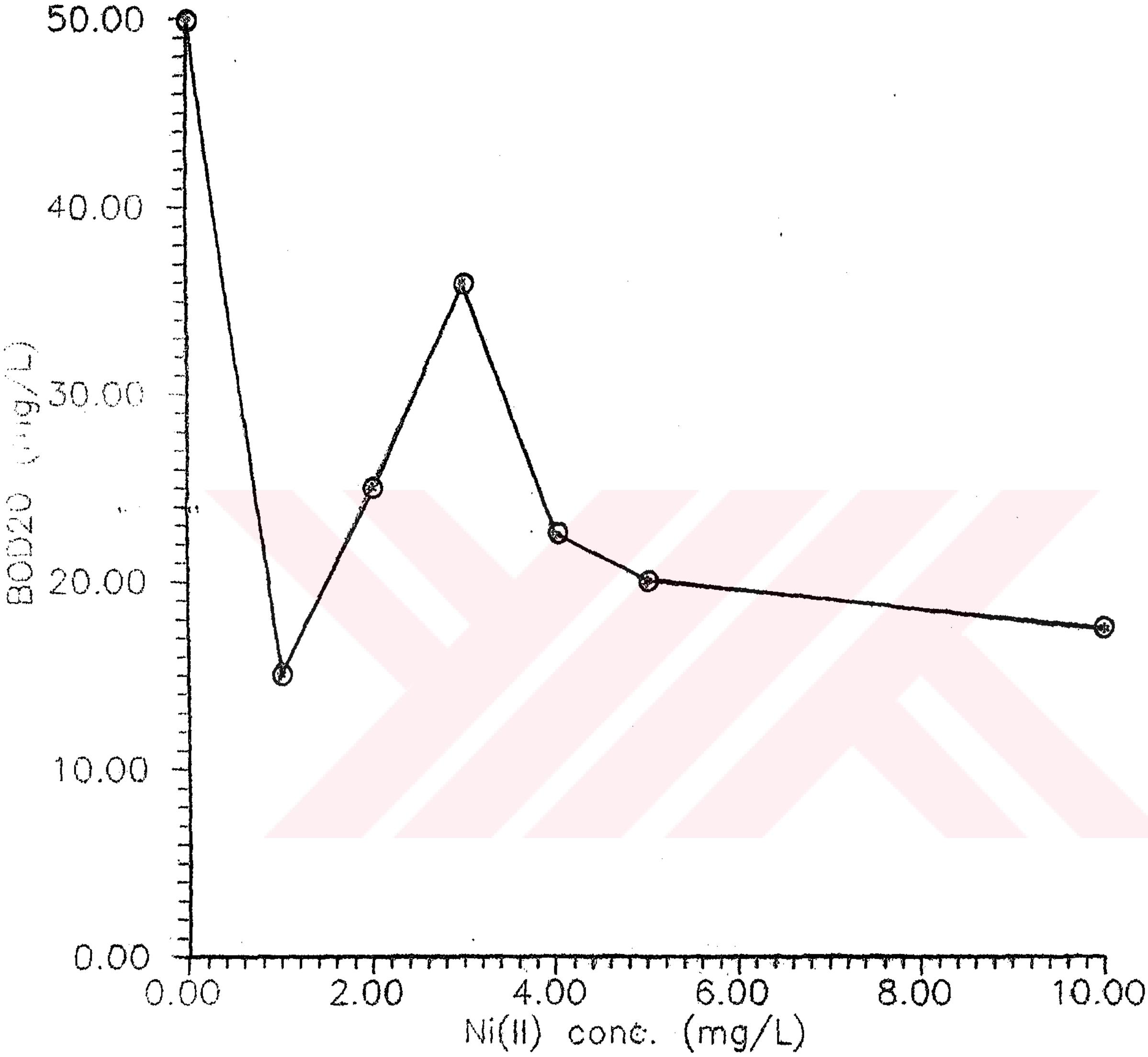


Figure 5.3. Effects of Ni(II) on BOD_{20}

Figure 5.4 shows the effect of Ni(II) on BOD_{20}, in the case of 1.0 and 3.0 mg/L data were not considered.

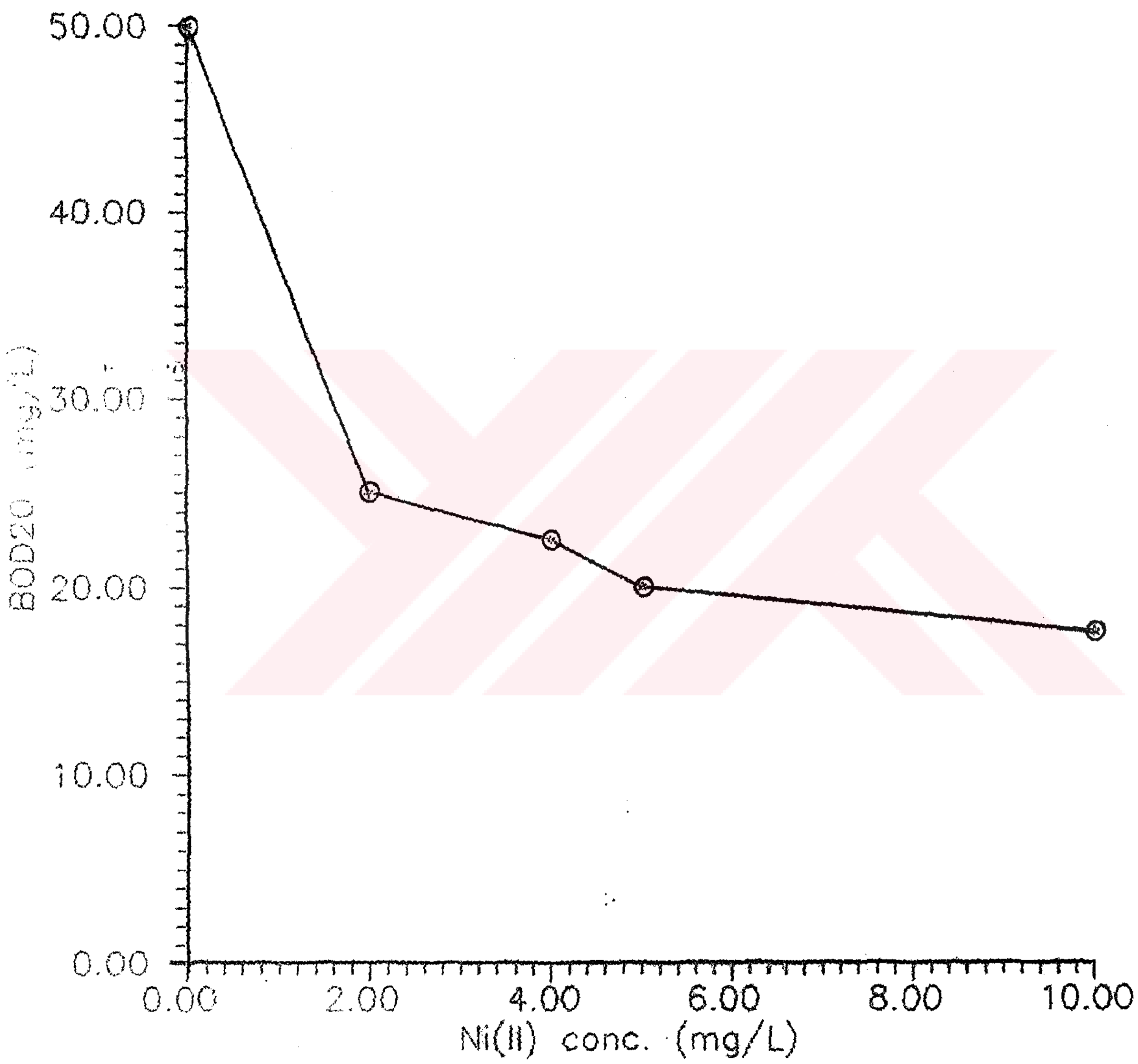


Figure 5.4. Effect of Ni(II) on BOD_{20} by omitting 1.0 and 3.0 mg/L Ni(II) data

5.2. Modelling of the BOD Curve

In order to quantify the effect of Ni(II) on BOD data and to test the validity of the model proposed by Swamee and Ojha (1991), the data presented in Appendix E and discussed in previous section were utilized.

The following sections are for the applicability of this model for BOD exertion in the presence of Ni(II). To this purpose, Swamee and Ojha's model was applied and the model parameters were determined for each Ni(II) concentration considered.

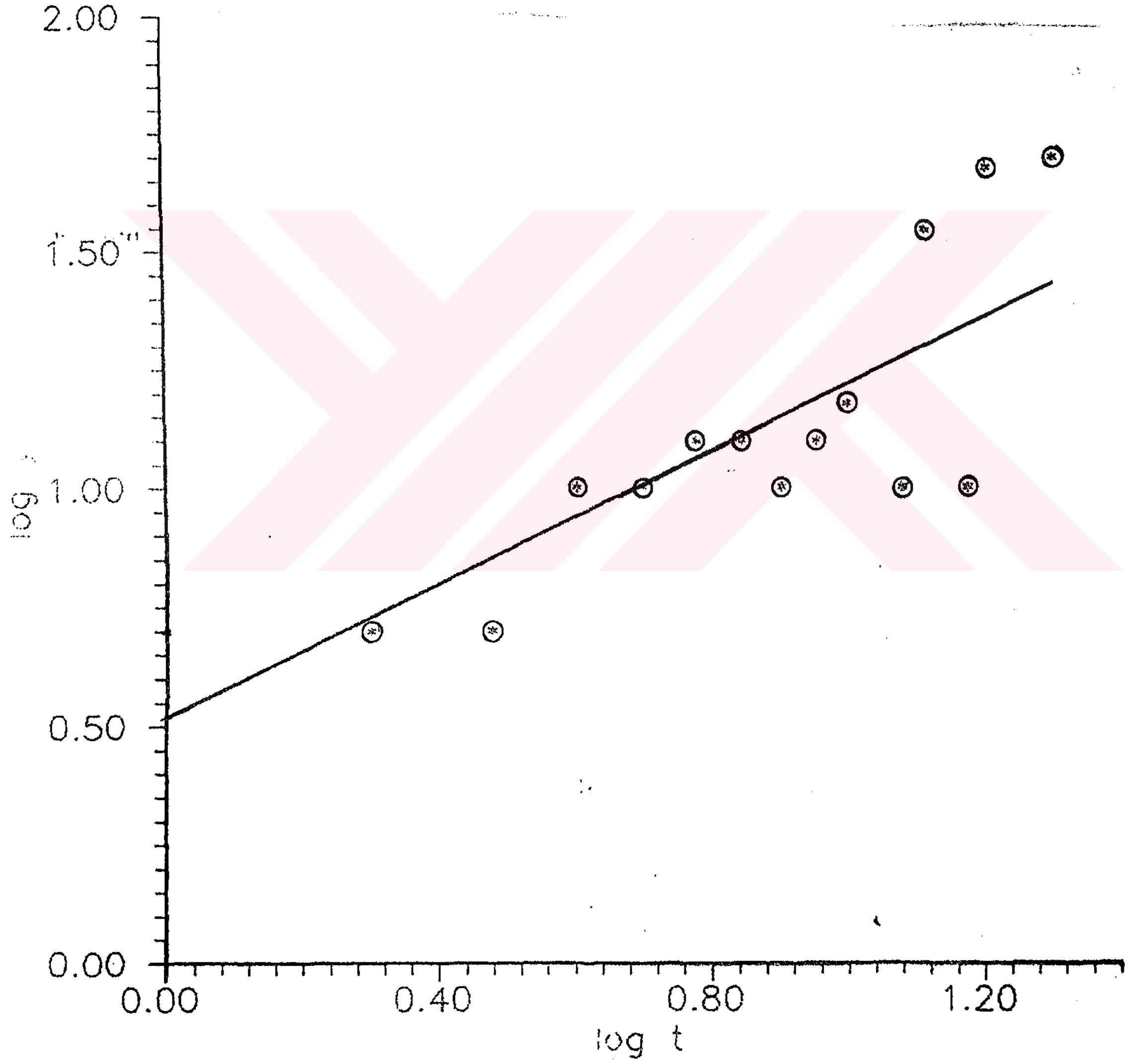
5.2.1. Applicability of the Model to the No-Nickel Case

Swamee and Ojha's model proposed for the carbonaceous BOD exertion of the wastewaters without any toxicant is:

$$y = L\,[(t_c/t)^{m_c/n} + 1]^{-n} \qquad (5.1)$$

As can be seen from equation (5.1), log y versus log t should yield a straight line if this model represents the data. The validity of this model for the synthetic wastewater considered (without Ni(II)) was tested by plotting BOD exertion "y" against time "t" on a logarithmic paper (Figure 5.5).

As it can be seen from Figure 5.5 and the correlation coefficient obtained, the fitness of the 0.0 mg/L data to the model proposed is acceptable. A straight line with a slope of 0.703 ± 0.2 and with an intercept of 0.517 ± 0.15 was fitted with a correlation coefficient of 0.80 to no Ni(II) BOD exertion data. Considering the nature of the Winkler BOD determination and the accuracy that can be obtained by this test, one can easily conclude that, the BOD exertion model proposed by Swamee and Ojha (1991) can be applied to data obtained in the absence of any toxicant. In other words; that is to prove the validity of this model for the synthetic wastewater utilized throughout this study. Rate exponent for the carbonaceous stage was found as 0.703 1/day from the slope of the straight line obtained.

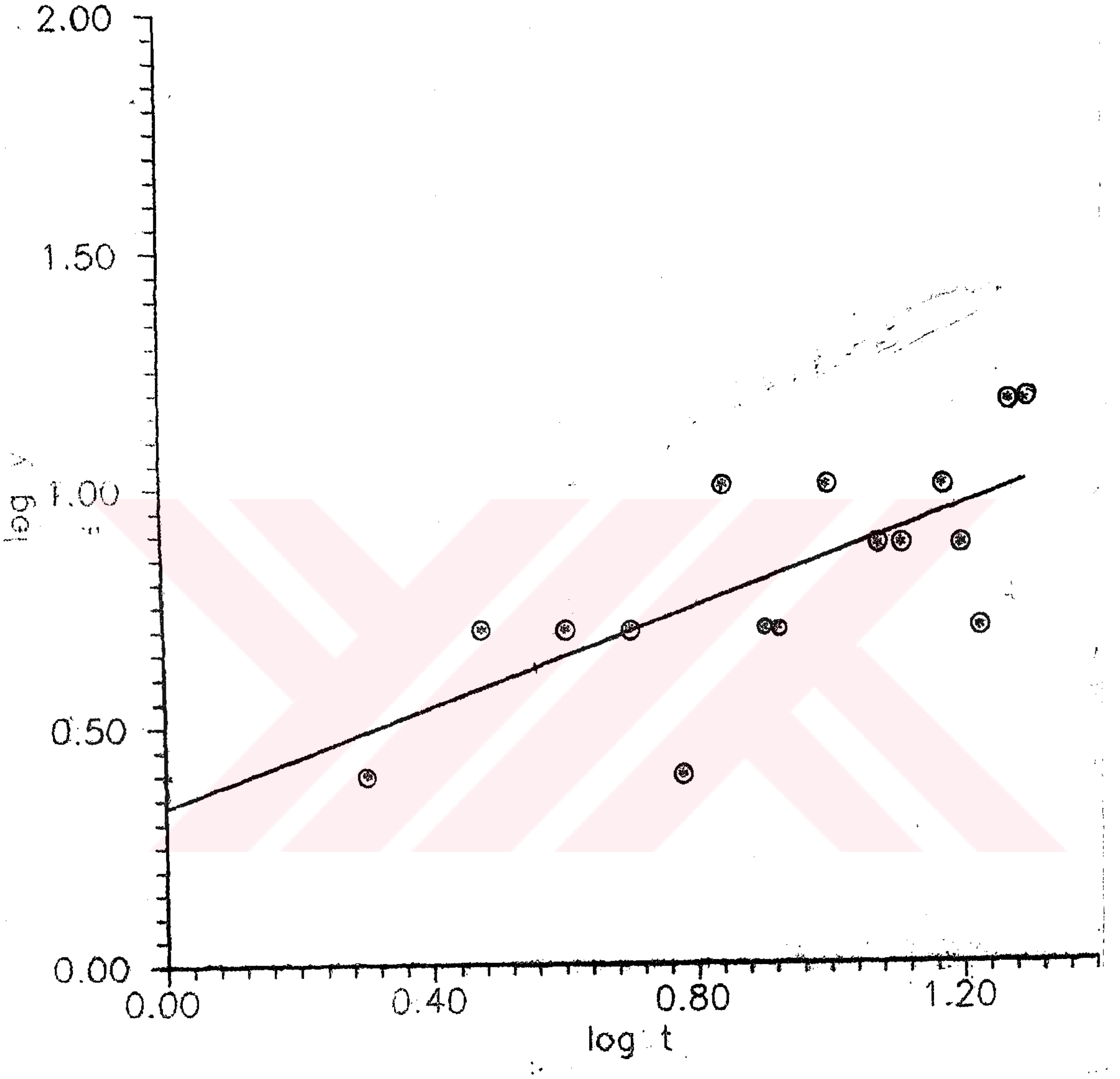


y = 0.702668t + 0.516516

Correlation Coefficient : 0.80

Figure 5.5. BOD Exertion in the Absence of Ni(II) (Log - Log Scale)

5.2.2. Applicability of Model to Wastewaters Bearing 1.0 mg/L Ni(II) Concentration



$y = 0.516197t + 0.333381$

Correlation Coefficient : 0.77

Figure 5.6. BOD Exertion in the Presence of 1.0 mg/L Ni(II) in the Wastewater

The BOD exertion model proposed by Swamee and Ojha (1991) for the wastewaters containing any toxicant is:

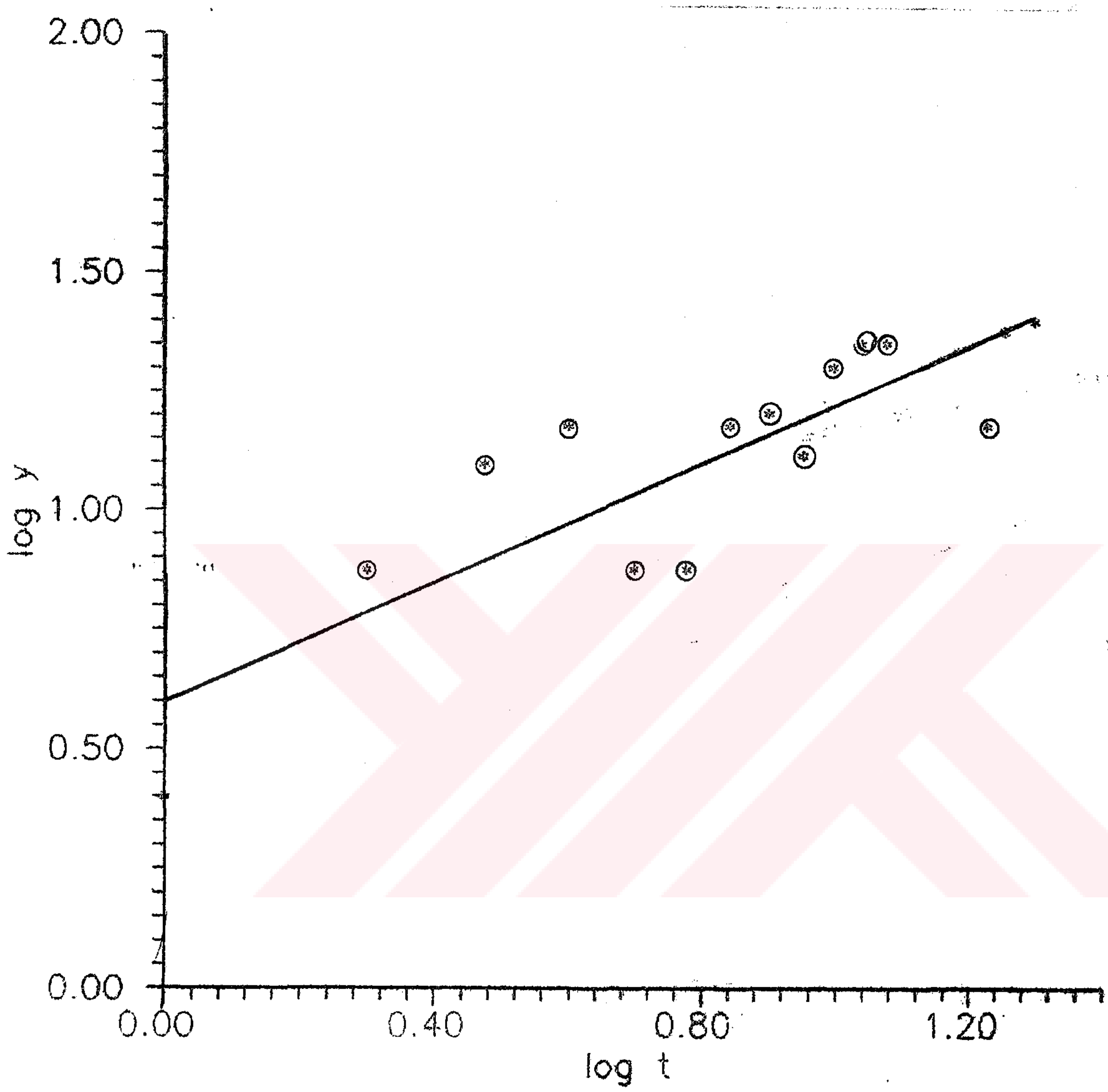
$$y=L[(t_L/t)^{m_L/n} + (t_c/t)^{m_c/n} + 1]$$

In this model, there is an additional term for the inclusion of the lag phase which is expected to take place in the presence of the toxicant. In this expression m_L is the rate exponent for the lag period whereas m_c is the rate exponent for the next phase or the phase after lag period. Therefore, it is normal to expect to have two straight lines with different slopes in log y versus log t plot in the presence of Ni(II).

In order to test the validity of this model for the wastewater bearing Ni(II) at a concentration of 1.0 mg/L, the data presented in Table E2 were utilized and Figure 5.6 was plotted. As can be seen from this figure, there is no lag phase in BOD exertion; microorganisms suddenly starts to oxidize the organic matter and continue to oxidizing the organic matter with the same rate exponent. Thus, there can be obtained a single straight line from log y versus log t plot with a slope of 0.516 ± 0.16 and with an intercept of 0.333 ± 0.11. The correlation coefficient obtained is 0.77. Since the magnitude of the correlation coefficient measures how well the data fits the model, the applicability of the model to the wastewater containing 1.0 mg/L Ni(II) is debatable. However considering the experimental errors which are not easy to prevent in Winkler BOD determination. It is not wrong to consider this value as acceptable. From the slope of the line, reaction rate came out to be 0.516 1/day which is less than that of no nickel case, namely, 0.703 1/day. This was contradictory to the findings of Yetiş (1988), who concluded that, Ni(II) at a concentration of 1 mg/L was stimulatory to the microbial activity in the BOD bottle. Considering this observation, at this Ni(II) concentration an increase in biological reaction rate could be expected, which is not observed in this study.

5.2.3. Applicability of Model to Wastewaters Bearing 2.0 mg/L Ni(II) Concentration

From Figure 5.7 it is obvious that, there is no lag in BOD exertion; BOD exertion starts immediately, and goes on following the same rate expression. Thus, there is a single line fitted to the log y versus log t data with a high correlation cooficient, 0.86. A comparison between 1.0 and 2.0 mg/L cases reveals that, the correlation obtained in 2.0 mg/L case is much better than 1.0 mg/L case. The slope of the straight line is 0.617 ± 0.14 and the intercept of it is 0.599 ± 0.1. From this straight line, rate exponent, m_c was found as 0.617 1/-day, which means that, 2 mg/L Ni(II) is inhibitory to the microbial activity in the BOD bottle. The percentage decrease in the rate exponent is about 12% with respect to no-Ni(II) case.



y = 0.617t + 0.599

Correlation Coefficent : 0.86

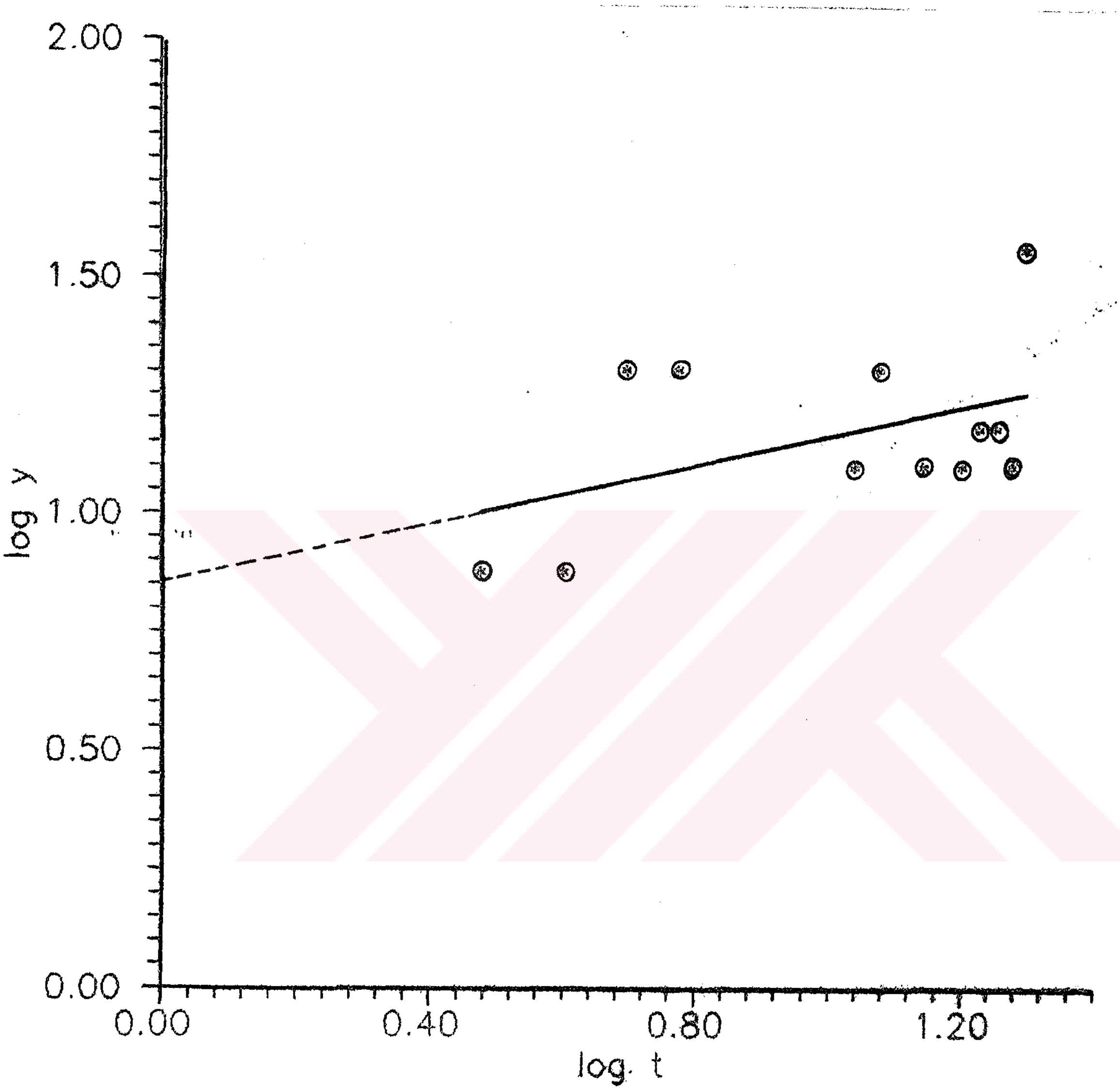
Figure 5.7. BOD Exertion in the Presence of 2.0 mg/L Ni(II) in the Wastewater

5.2.4. Applicability of Model to Wastewaters Bearing 3.0 mg/L Ni(II) Concentration

As in the cases of 1.0 and 2.0 mg/L Ni(II), lag phase also, could not be observed in the presence of 3.0 mg/L Ni(II) in the wastewater. So, a single line with a slope of 0.306 ± 0.18 and with an intercept of 0.854 ± 0.18 was plotted. As it can be easily seen from Figure 5.8 considerable deviations of the data from the best fit line shows a very bad correlation, 0.47. A very low rate constant, m_c, compared to 0.0, 1.0 and 2.0 mg/L Ni(II) cases was calculated which is 0.306 1/day. However, these unsatisfactory results may be partly attributed to experimental errors mentioned in Section 5.1.2.

5.2.5. Applicability of Model to Wastewaters Bearing 4.0 mg/L Ni(II) Concentration

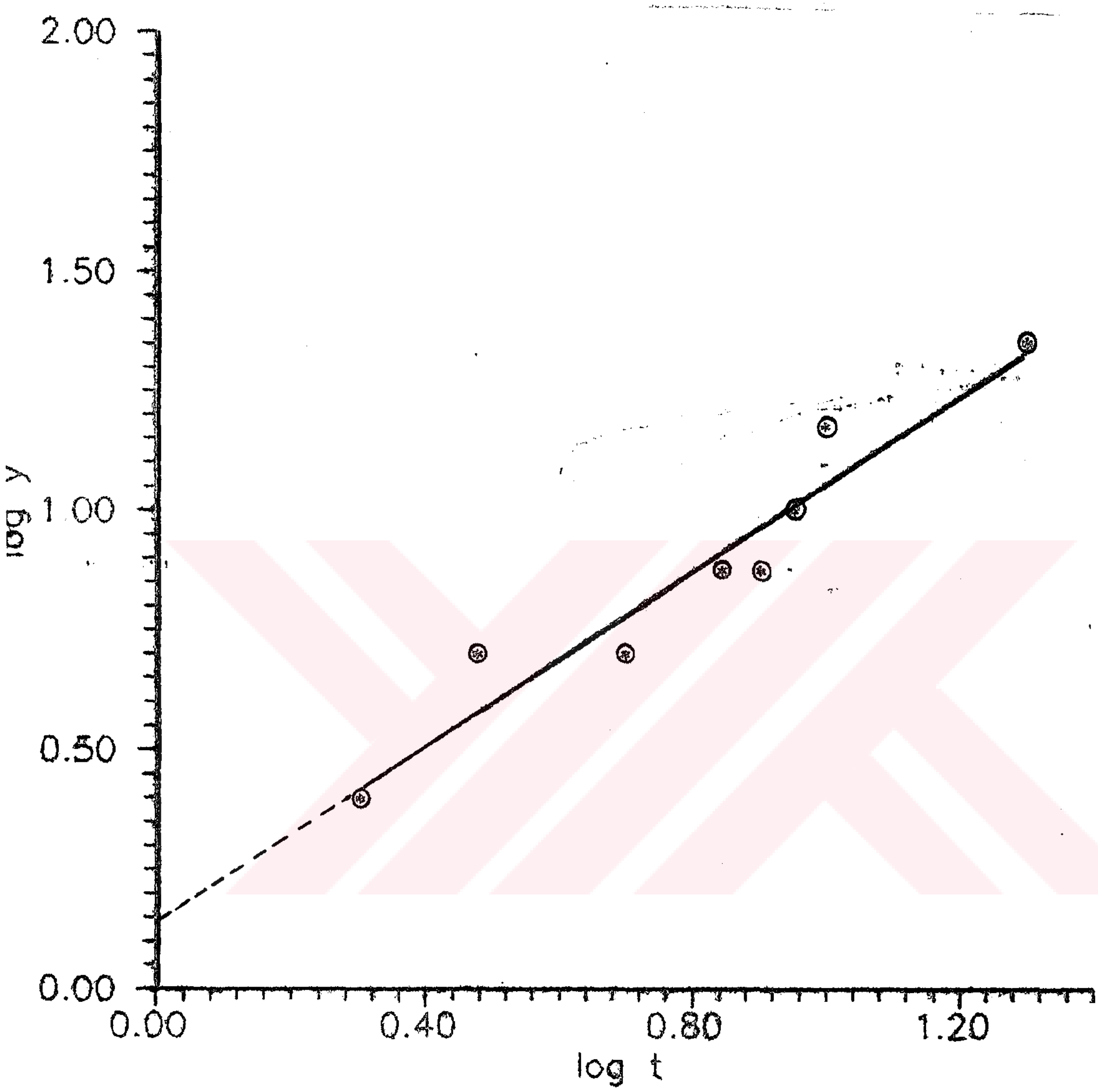
During the experiments run with the 4 mg/L Ni(II) concentration, BOD exertion started initially and showed an increasing rate kinetics. Thus, as in other cases, one straight line with one slope was obtained (Figure 5.9). The reaction rate m_c, namely, 0.913 1/day shows that, 4 mg/L Ni(II) is inhibitory to the microbial activity in the BOD bottle. This is confirmed by the findings of Yetiş (1988), such that, higher reaction rate was found than that of no-Ni(II) case,which is 0.703 1/day. A comparison with the other Ni(II) concentrations, 0.0, 1.0, 2.0, and 3.0 mg/L reveals that the correlation obtained in 4.0 mg/L is the best one obtained.



y = 0.306t + 0.854

Correlation Coefficient : 0.47

Figure 5.8. BOD Exertion in the Presence of 3.0 mg/L Ni(II) in the Wastewater

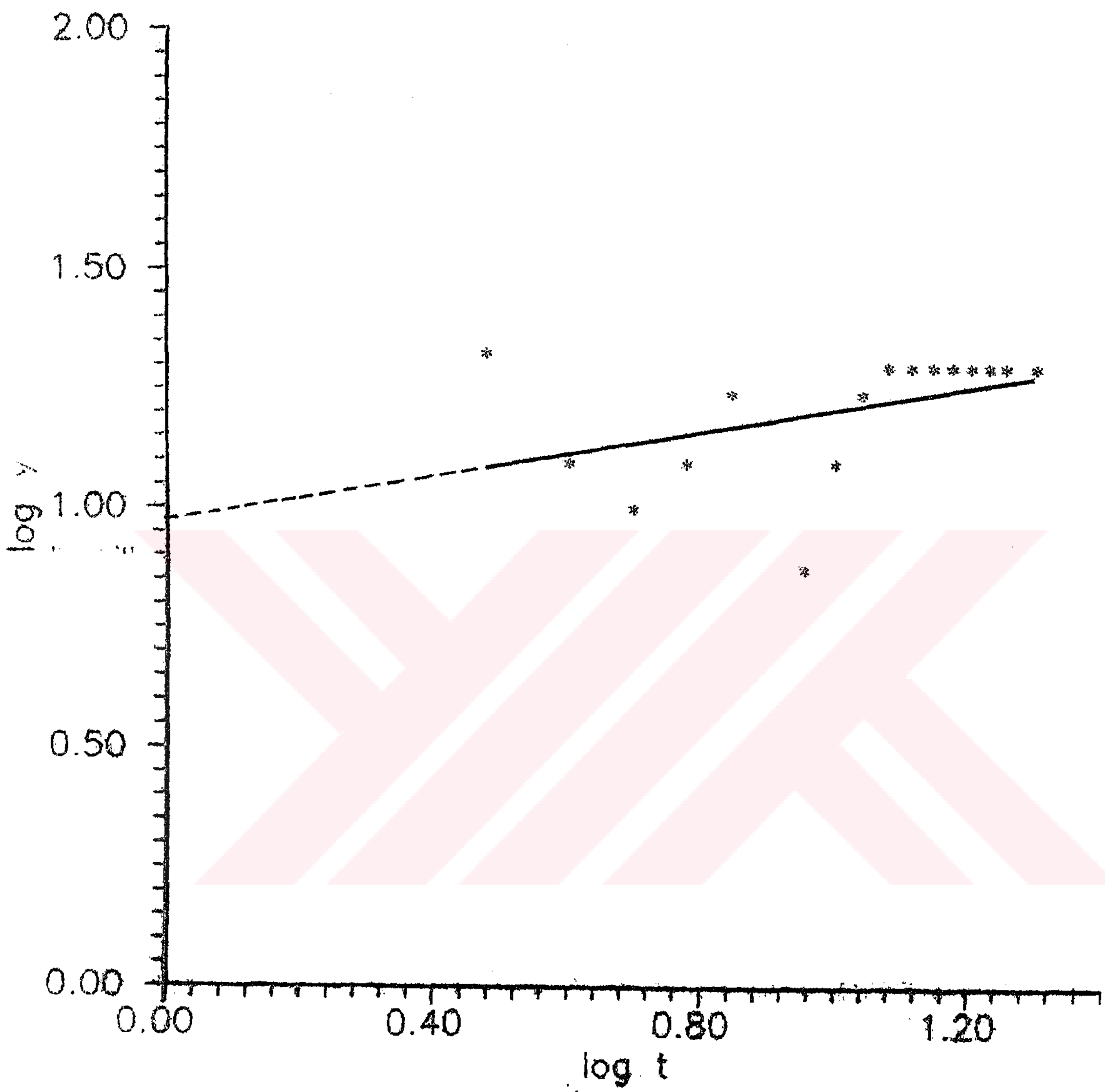


y = 0.913t + 0.144

Correlation Coefficient : 0.96

Figure 5.9. BOD Exertion in the Presence of 4.0 mg/L Ni(II) in the Wastewater

5.2.6. Applicability of Model to Wastewaters Bearing 5.0 mg/L Ni(II) Concentration



y = 0.239t + 0.972

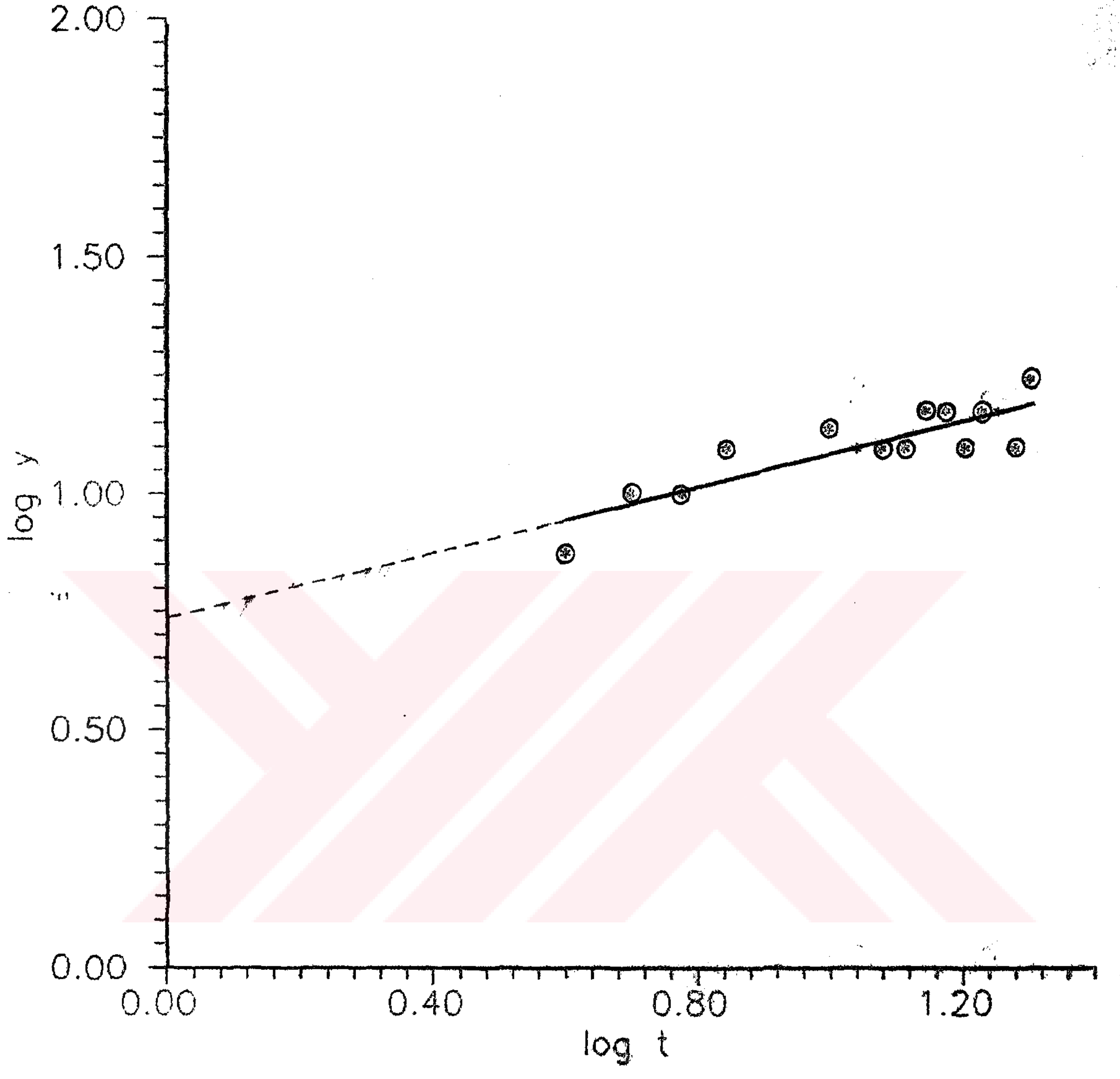
Correlation Coefficient : 0.44

Figure 5.10. BOD Exertion in the Presence of 5.0 mg/L Ni(II) in the Wastewater

Figure 5.10 obviously shows the deviations of the data from the best fit line with a correlation coefficient of 0.44. This means a model proposed by Swamee and Ojha (1991) can not be applied to wastewaters bearing 5.0 mg/L Ni(II) concentrations. Rate exponent is found to be 0.239 1/day, which shows 66% decrease from the rate exponent of no Ni(II) case.

5.2.7. Applicability of Model to Wastewaters Bearing 10.0 mg/L Ni(II) Concentration

From Figure 5.11. it is obvious that, there is no lag in BOD exertion; BOD exertion starts immediately, and goes on following the same rate expression. Thus, there is a single line fitted to the log y versus log t data with a high correlation cooficient, which is 0.86. A comparison with other Ni(II) concentrations considered reveals that, the correlation obtained in 10.0 mg/L case is much better than 1.0, 3.0, 5.0 mg/L cases. The slope of the straight line is 0.353 ± 0.04 and the intercept of it is 0.732 ± 0.06. From this straight line, rate exponent, m_c was found as 0.353 1/day, which means that, 10 mg/L Ni(II) is inhibitory to the microbial activity in the BOD bottle.



y = 0.353t + 0.732

Correlation Coefficient : 0.86

Figure 5.11. BOD Exertion in the Presence of 10.0 mg/L Ni(II) in the Wastewater

5.3. Evaluation of BOD Exertion For Various Ni(II) Concentrations

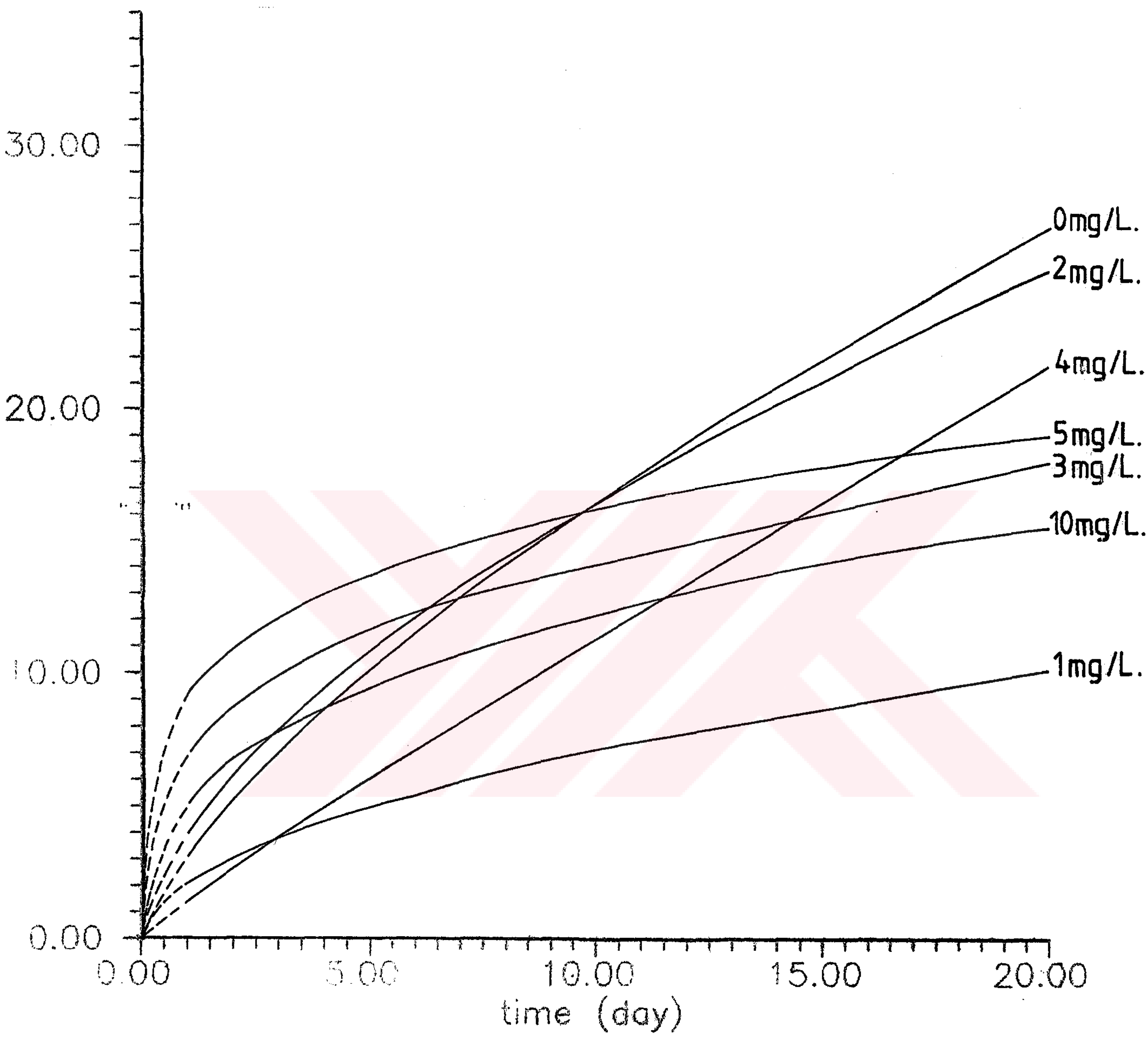


Figure 5.12. BOD Exertion Curves of Different Ni(II) Concentrations

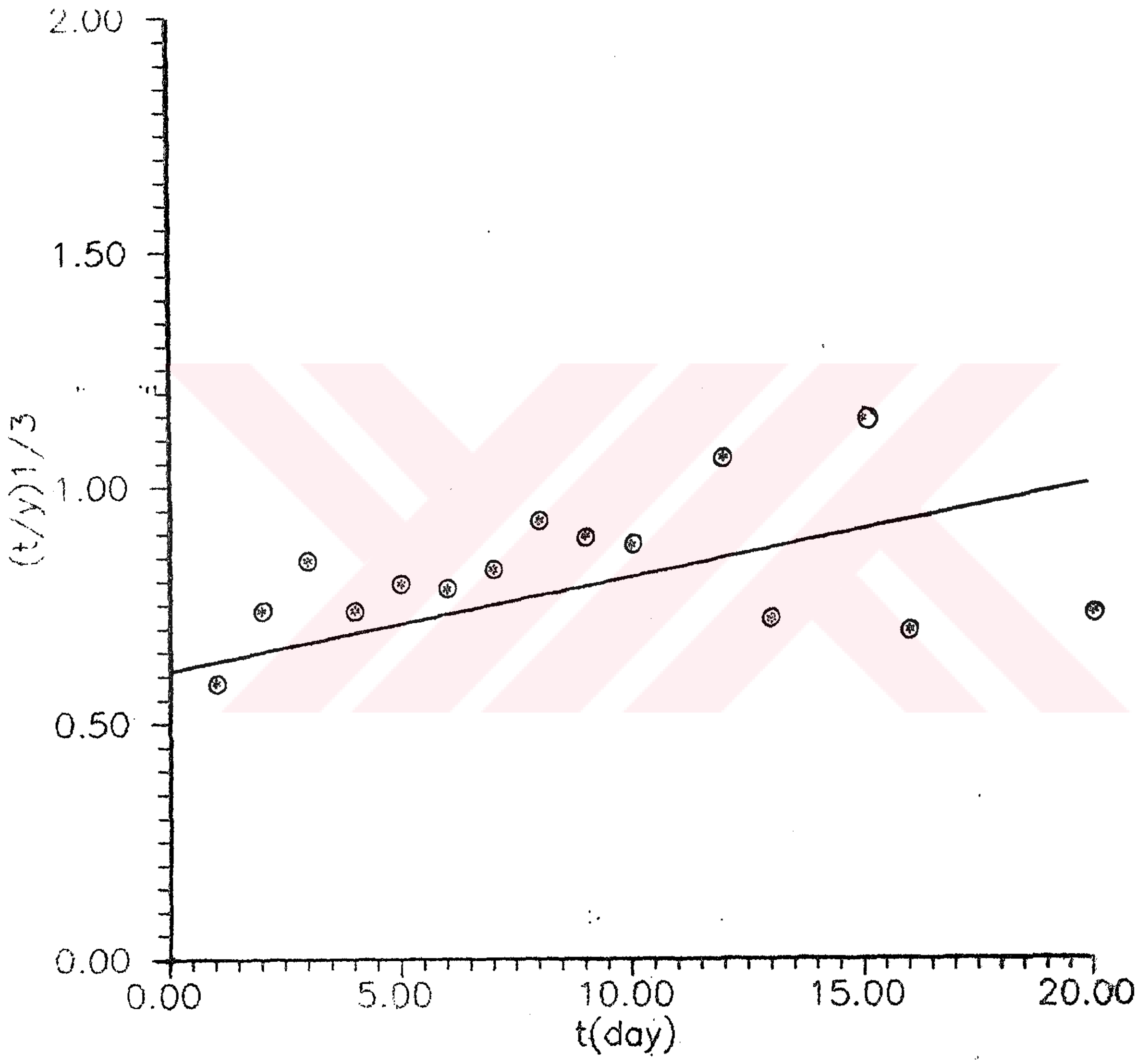
As mentioned before, the BOD values may have the risk of not reflecting the true strength of the influent in the presence of heavy metals as is indicated in Figure 5.12, which shows the resulting BOD exertion curves obtained throughout this study. The BOD exertion curves indicated in this figure are the drawings of the equations presented in Figures (5.5 5.11). As is obvious from Figure 5.12, 1.0 mg/L and 3.0 mg/L Ni(II) data did not satisfy our expectations, such that, the ultimate BOD value of 1.0 mg/L Ni(II) concentration is lower than that of 10.0 mg/L and ultimate BOD of 3.0 mg/L is lower than that of 5.0 mg/L. The reason for these two exceptional BOD data can be attributed to the experimental errors. Throughout the experimental study, measurements for 1.0 and 3.0 mg/L Ni(II) concentrations were conducted together within the same set of experiment, which might be performed with a relatively low organic strength wastewater by experimental error.

5.4. Thomas Method for the Estimation of BOD Parameters, k and L

In this study, k and L values were also calculated using Thomas method to compare ultimate BOD values obtained by this method and from Swamee and Ojha's (1991) model. In fact, the purpose in this approach was to compare the models rather than the numerical results obtained.

In order to test the validity of the Thomas method for the wastewater without Ni(II) and to calculate the parameters k and L, the data presented in Table E1 was used. A straight line with a slope of 0.02 ± 0.23, with an intercept of 0.609 ± 0.01 was fitted to t versus $(t/y)^{1/3}$ transformation of data

(Figure 5.13). However, the correlation coefficient of this fit was a quite low value, namely, 0.47. From the equation of this line, reaction rate, k, and ultimate BOD, L, estimated as 0.1976 1/day and 22.45 mg/L respectively.

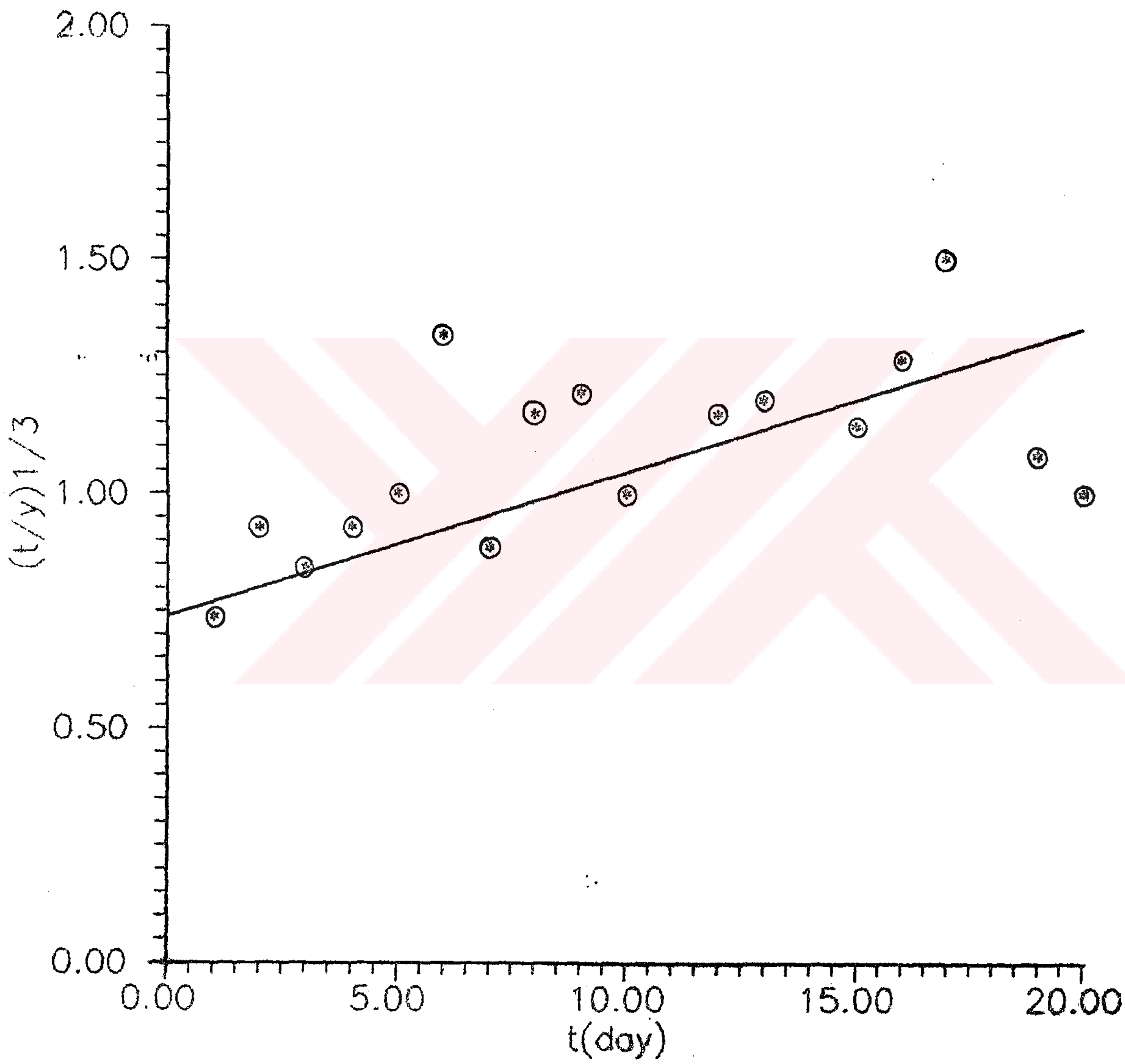


$y = 0.02t + 0.609$

Correlation Coefficient: 0.47

Figure 5.13. t versus $(t/y)^{1/3}$ Transformation of Data in the Absence of Ni(II)

Similarly, for 1.0 mg/L Ni(II) concentration, a straight line with a slope of 0.031 ± 0.26 and with an intercept of 0.739 ± 0.01 was fitted to the data presented in Table E2 (Figure 5.14). Reaction rate was calculated as 0.249 1/day and ultimate BOD was found as 9.92 mg/L.

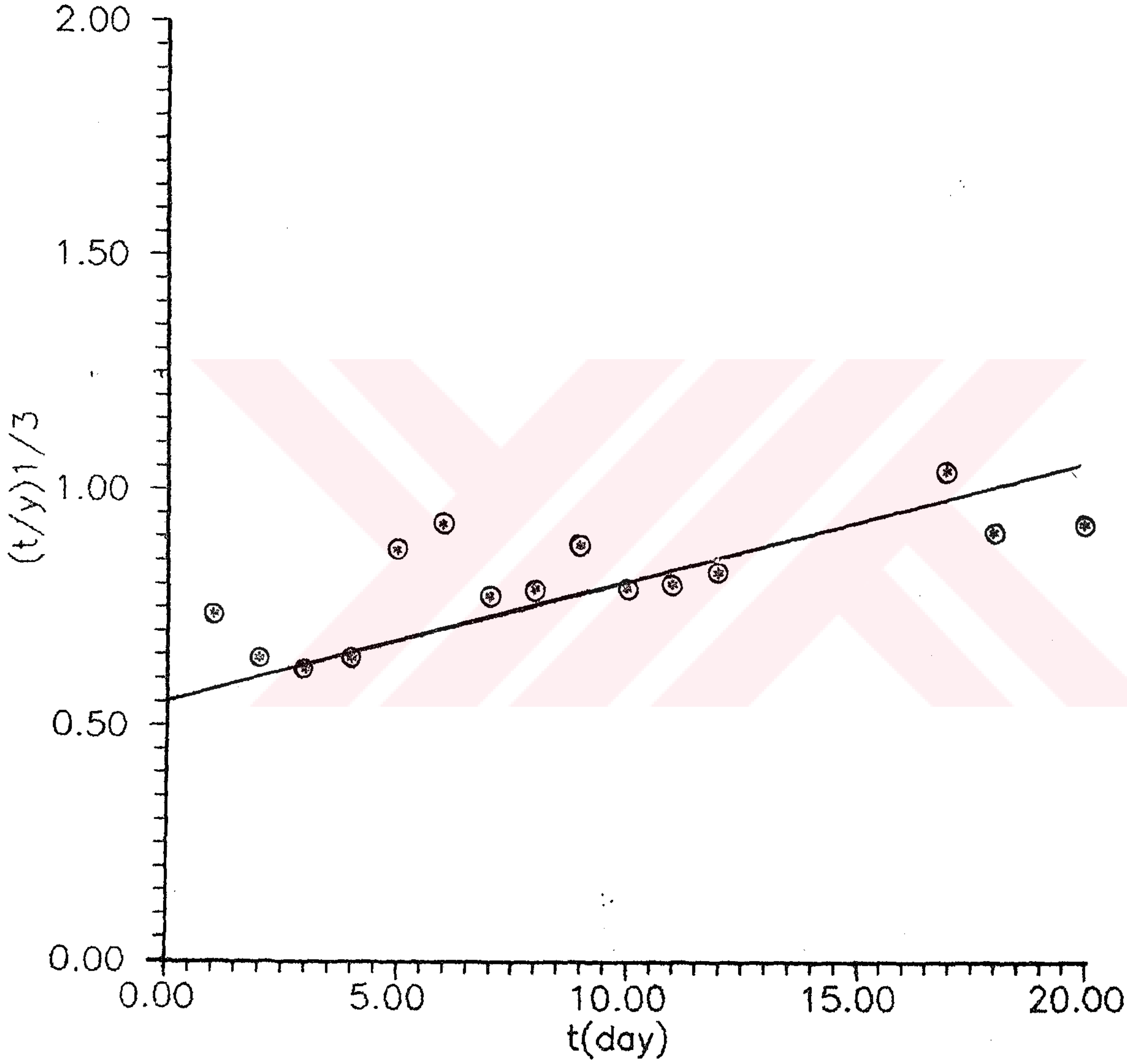


y = 0.031t + 0.739

Correlation Coefficient: 0.61

Figure 5.14. t Versus $(t/y)^{1/3}$ Transformation of Data for the Wastewaters Bearing 1.0 mg/L Ni(II) Concentration

For 2.0 mg/L Ni(II containing wastewater, similar straight line with a slope of 0.025 ± 0.18 and intercept of 0.553 ± 0.008 was fitted with a correlation coefficient of 0.70(Figure 5.15). From the equation of this line, k was calculated as 0.273 1/day and L was calculated as 21.557 mg/L.

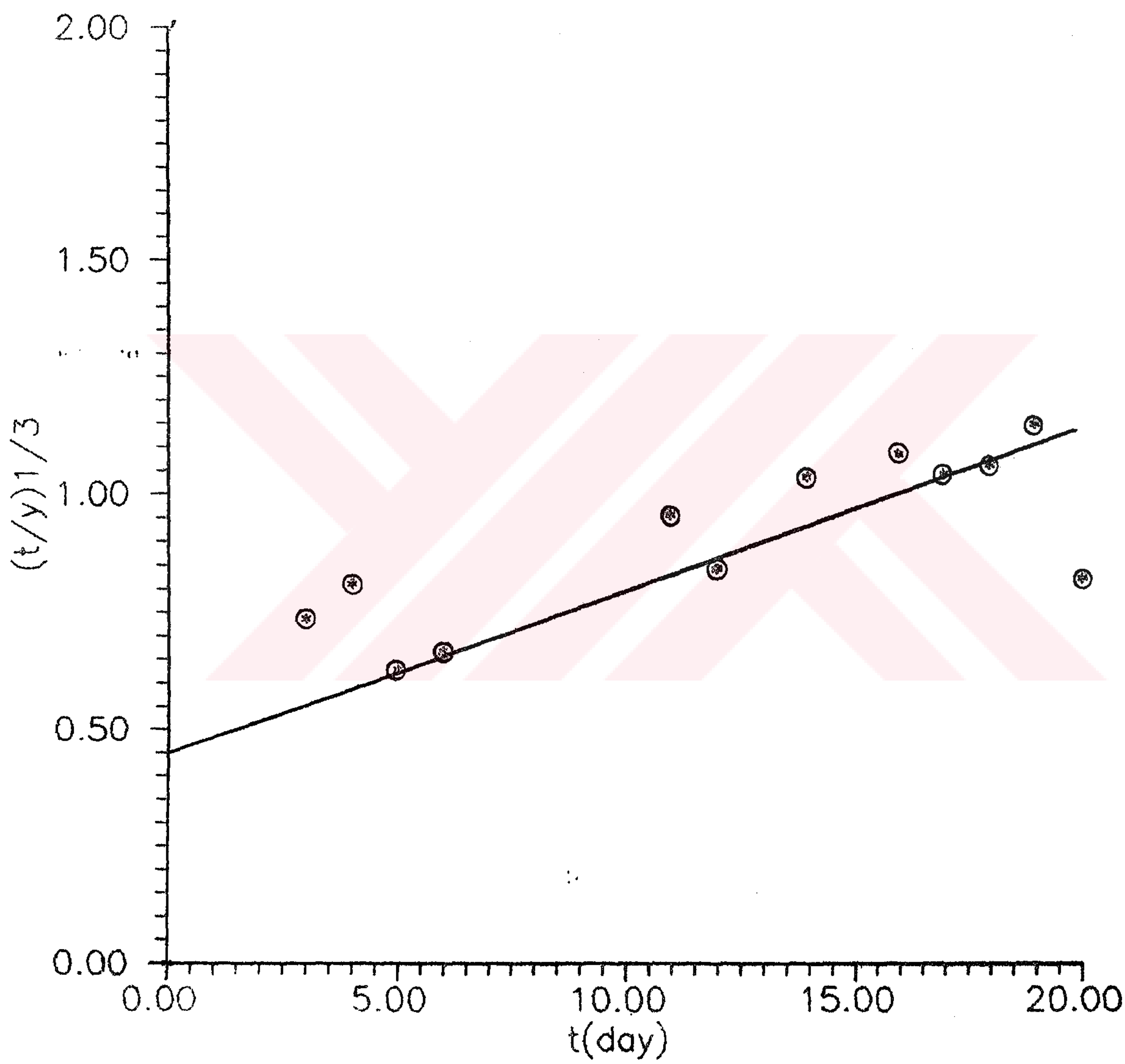


y = 0.025t + 0.553

Correlation Coefficient: 0.70

Figure 5.15. t Versus $(t/y)^{1/3}$ Transformation of Data for the Wastewaters Bearing 2.0 mg/L Ni(II) Concentration

For the wastewater bearing 3.0 mg/L Ni(II), the data given in Table E4 was used, and a straight line with a slope of 0.0345 ± 0.12, with an intercept of 0.45 ± 0.006 and with a coefficient of correlation 0.77 was drawn (Figure 5.16). From this fit k and L were calculated as 0.46 1/day and 23.88 mg/l respectively.

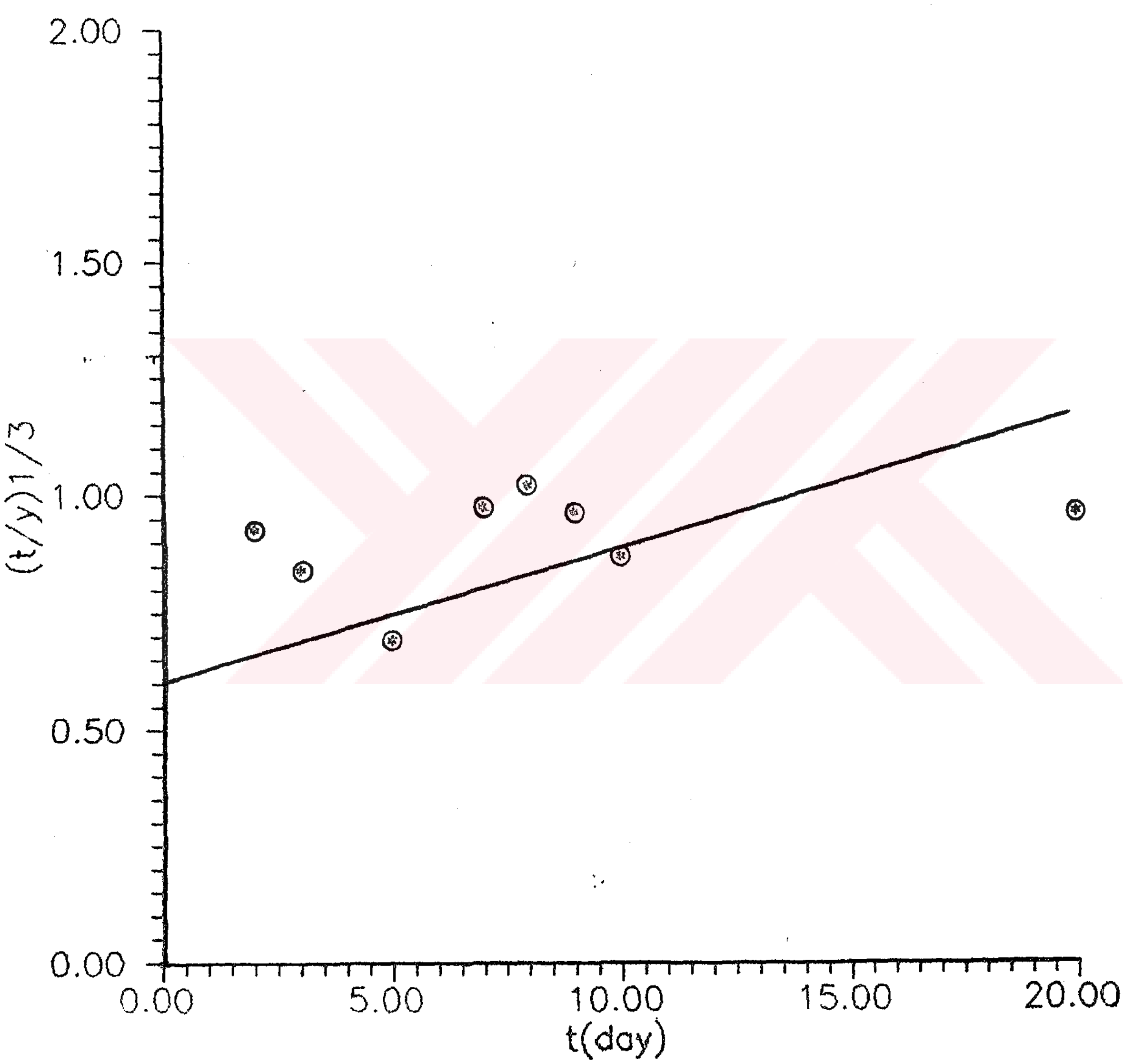


y = 0.0345t + 0.45

Correlation Coefficient: 0.77

Figure 5.16. t Versus $(t/y)^{1/3}$ Transformation of Data for the Wastewaters Bearing 3.0 mg/L Ni(II) Concentration

Similarly, for 4.0 mg/L Ni(II) concentration a straight line with a slope of 0.028 ± 0.29 and with an intercept of 0.605 ± 0.02 was fitted to the data presented in Table E5 (Figure 5.17). Reaction rate was calculated as 0.281 1/day and ultimate BOD was found as 16.04 mg/L.

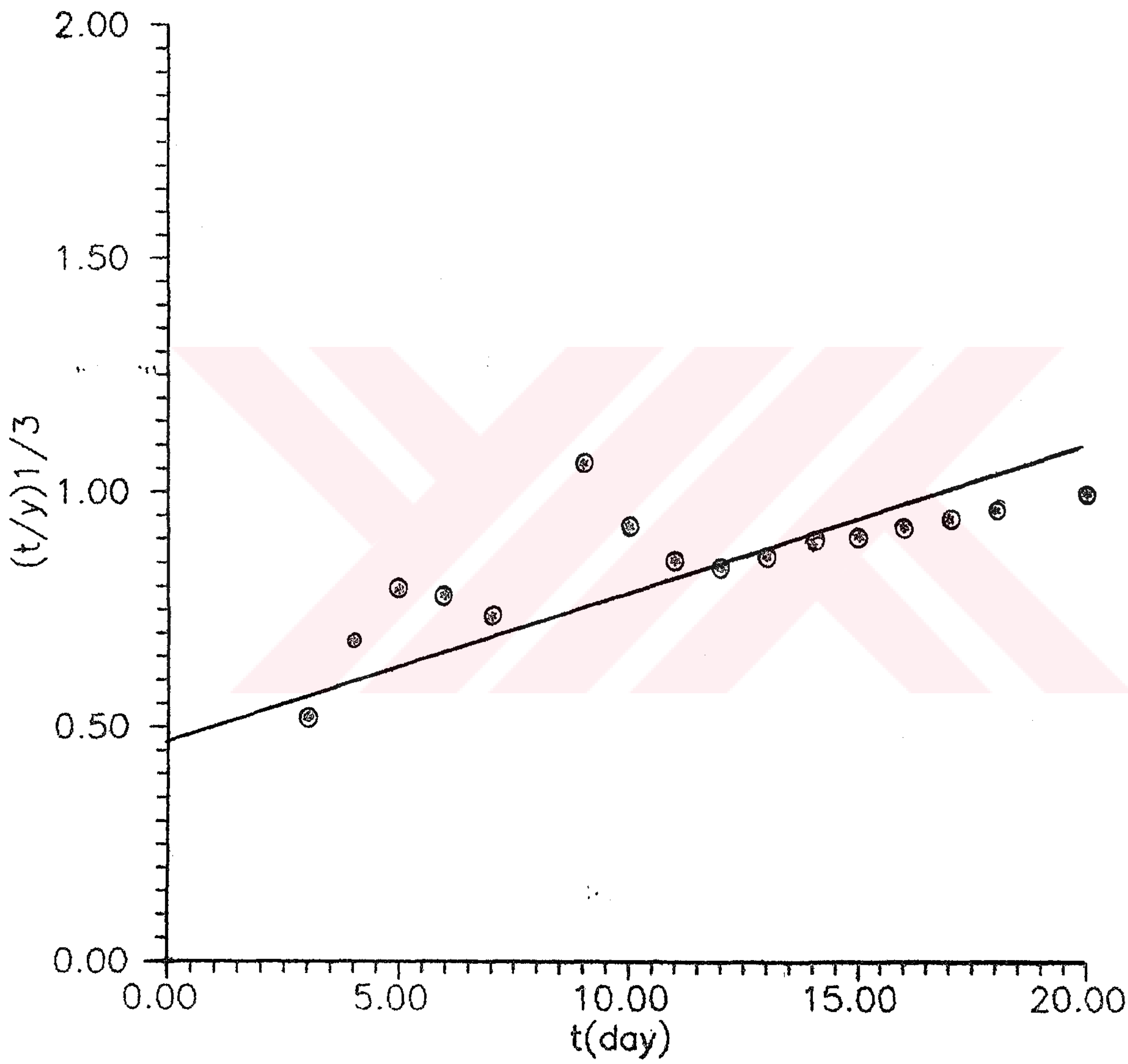


y = 0.028t + 0.605

Correlation Coefficient: 0.53

Figure 5.17. t Versus $(t/y)^{1/3}$ Transformation of Data for the Wastewaters Bearing 4.0 mg/L Ni(II) Concentration

A straight line having the slope of 0.32 ± 0.167 and intercept of 0.47 ± 0.007 was fitted for wastewater bearing 5.0 mg/L Ni(II) concentration according to data presented in Table E6 (Figure 5.18). From the equation of the line, k and L were calculated 0.405 1/day and 23.71 mg/L, respectively.

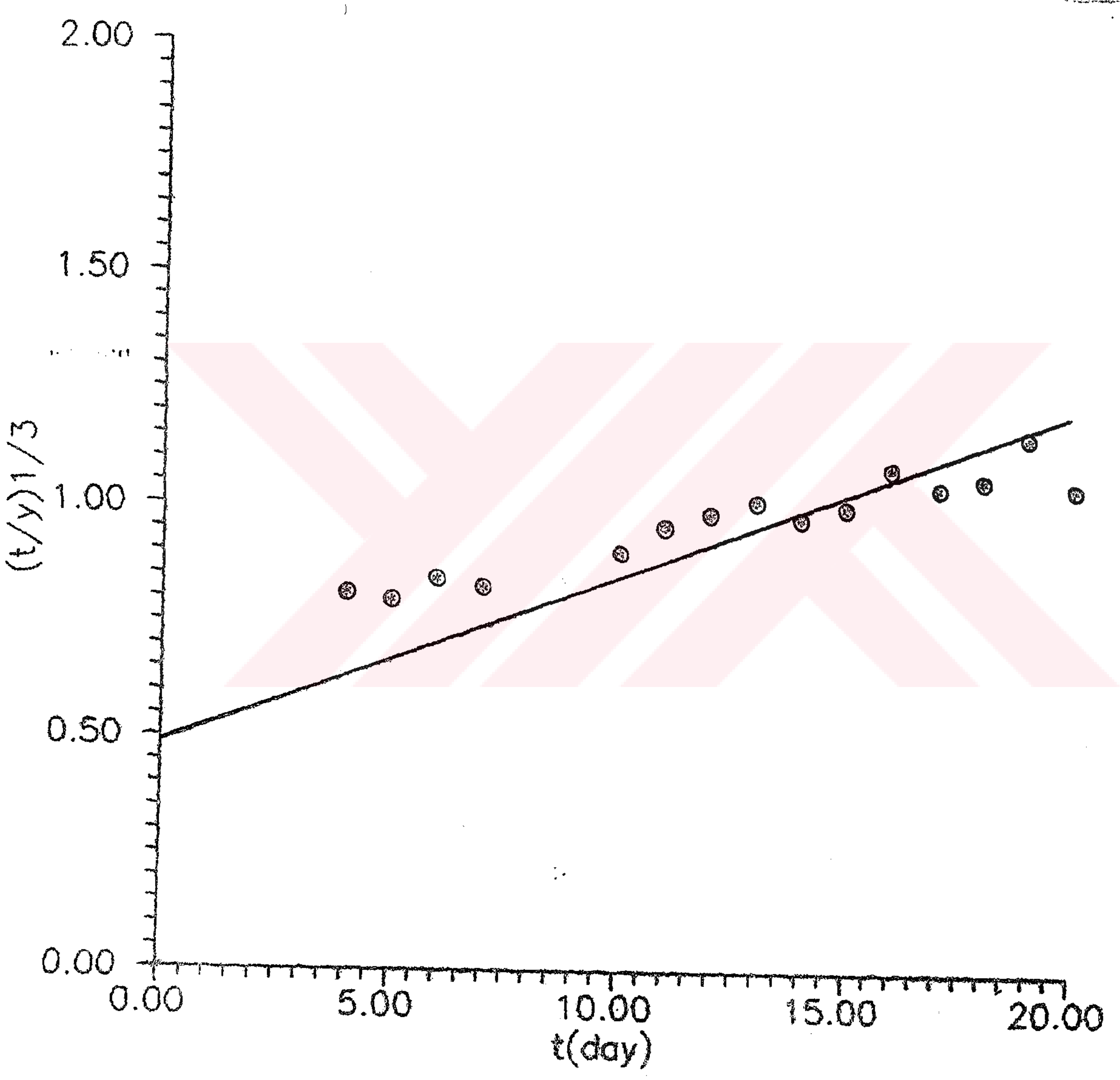


y = 0.032t + 0.47

Correlation Coefficient: 0.75

Figure 5.18. t Versus $(t/y)^{1/3}$ Transformation of Data for the Wastewaters Bearing 5.0 mg/L Ni(II) Concentration

Finally, for the wastewaters containing 10.0 mg/L Ni(II) concentration using the data given in Table E7, a straight line with a slope of 0.036 ± 0.16, with an intercept of 0.486 ± 0.002 and with a correlation coefficient of 0.81 was obtained. Reaction rate, k was found as 0.443 1/day and ultimate BOD as 19.643 mg/L (Figure 5.19).



y = 0.036t + 0.486

Correlation Coefficient: 0.81

Figure 5.19. t Versus $(t/y)^{1/3}$ Transformation of Data for the Wastewaters Bearing 10.0 mg/L Ni(II) Concentration

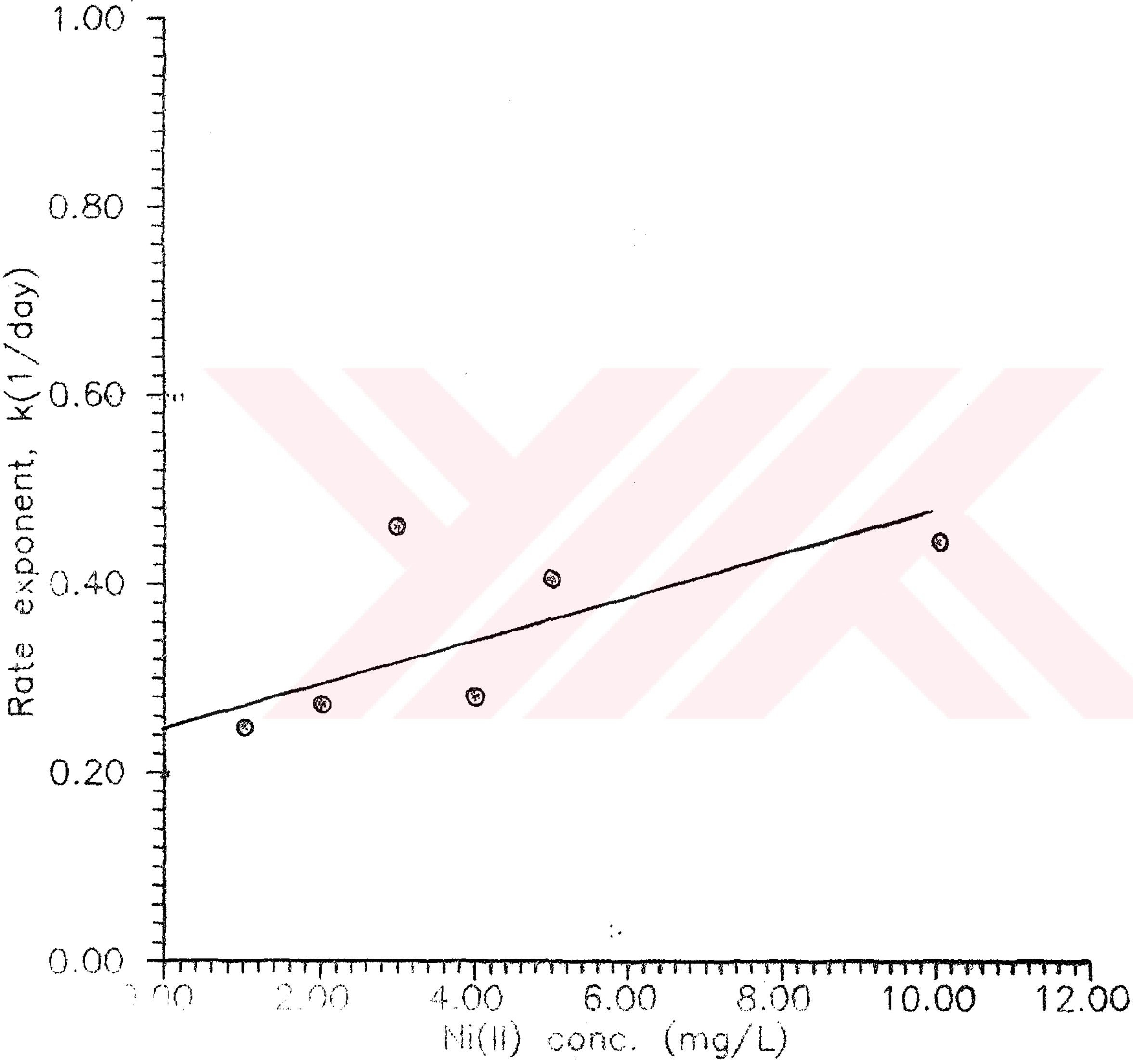


Figure 5.20.Variation of k with Ni(II) Concentration

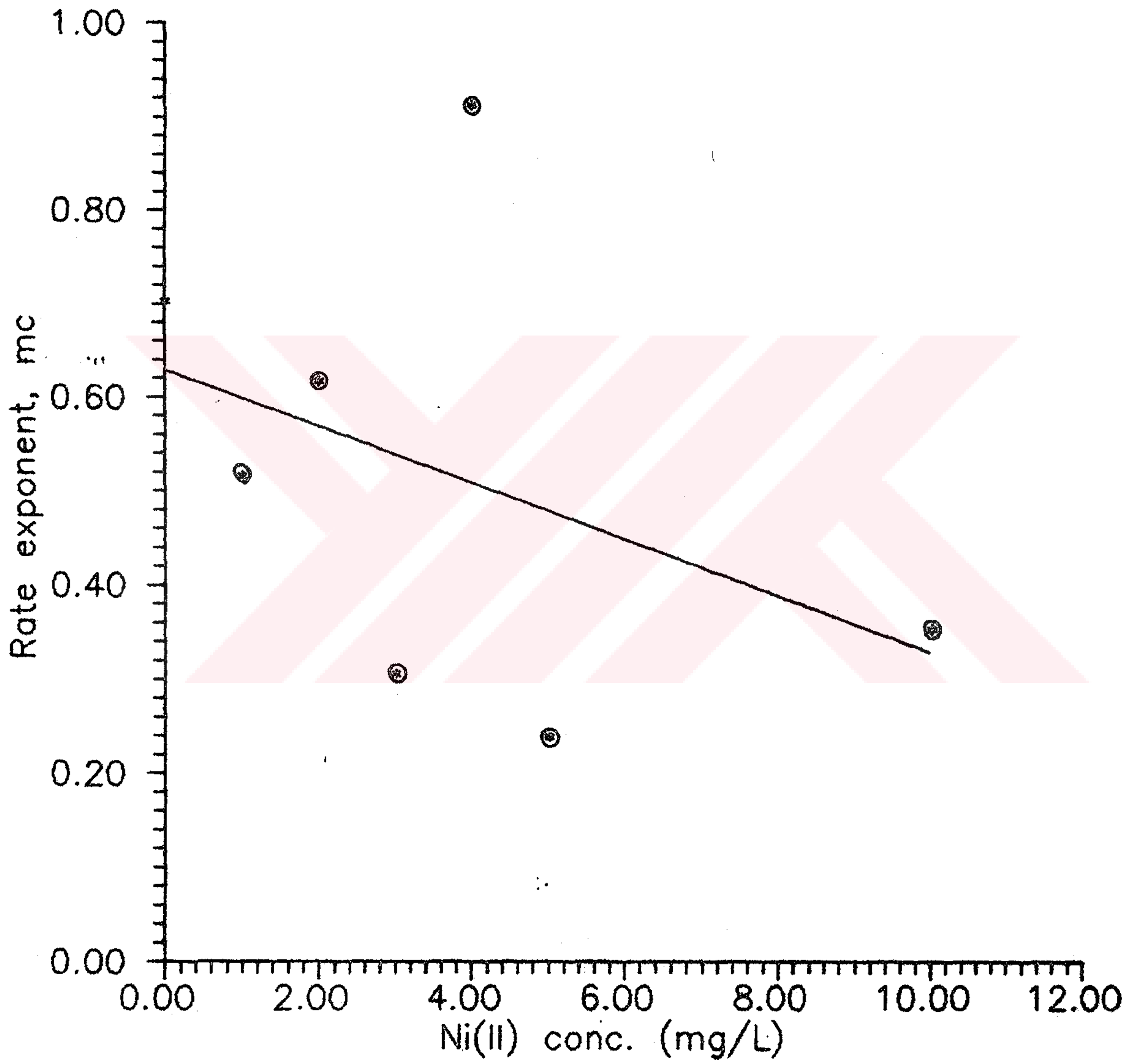


Figure 5.21. Variation of m_c with Ni(II) Concentration

Assessment of the above evaluations on the validity of Thomas method for the BOD exertion in the presence of Ni(II) have indicated that; Thomas method does not give us satisfactory results for the prediction of k and L as expected. This is obvious for the correlation coefficients obtained from each Ni(II) concentrations. As it was discussed in previous paragraphs, the correlation coefficients for the Thomas method is never above 0.81. That is a relatively low value. Furthermore, it is expected to have decreasing BOD ultimate values with increasing heavy metal concentration. However, as it is presented in Table 5.6, there are fluctuations in L values with increasing Ni(II) concentrations. Thus, it is possible to conclude that, Thomas method is not so satisfactory in predicting the BOD parameters for the wastewaters bearing Ni(II).

When the Thomas method is examined from the point of view of the reaction rate constant, k, very interesting but confusing results are obtained. As can be seen from Figure 5.20, reaction rate constant obtained by Thomas method, increase with increasing Ni(II) concentrations. However, this is contradictory to our experimental findings (Figure 5.21). Normally, it is expected to have a decrease in k with increasing Ni(II) concentrations as in the case of Swamee and Ojha (1991) model. The following section is for the comperative evaluation of these two models and their effectiveness in prediction of BOD exertion in the presence of Ni(II).

5.5. Comparison of Swamee and Ojha Model and Thomas Method

From the application of Swamee and Ojha model to experimental results obtained in this study, the reaction rate constant, m_c was evaluated for each Ni(II) concentration. Figure 5.21 is a plot which shows th change in m_c with Ni(II) concentration. The reaction rate constant is 0.702 1/day for 0.0 mg/L Ni(II) concentration; and it gradually decreases to about 0.28 1/day for a Ni(II) concentration of 4.0 mg/L. Beyond this Ni(II) concentration, the reaction rate constant is almost steady and it is about 0.24 1/day for 10.0 mg/L.

Contradictory to this findings, from the application of Thomas method, increasing reaction rates were observed with increasing Ni(II) concentration.

Since it is impossible to give reliable results only according to the correlation coefficients and to strengthen the above discussions on the comparison of validities of both Swamee and Ojha model and Thomas method, the deviations of the calculated L values from the observed BOD measurements were plotted (see Appendix F).

Table 5.6 summarizes the BOD parameters calculated by both Swamee and Ojha model and Thomas method.

Table 5.6. Comparison of BOD Parameters Calculated by Thomas Method and Swamee and Ojha's Model

Ni(II) conc. (mg/L)	L(mg/L) From model	L(mg/L) From Thomas met.	m_c (1/day)	k (1/day)
0.00	26.98	22.45	0.702	0.198
1.00	10.12	9.92	0.516	0.249
2.00	25.30	21.60	0.617	0.273
3.00	18.30	23.88	0.306	0.460
4.00	21.51	16.04	0.913	0.281
5.0	19.15	23.71	0.239	0.405
10.0	15.54	19.64	0.353	0.443

CHAPTER VI

CONCLUSION

In this study, the effect of Ni(II) on BOD exertion and the modelling of the BOD exertion curve in the presence of Ni(II) was evaluated. Different levels of Ni(II), namely, 1.0, 2.0, 3.0, 4.0, 5.0 and 10.0 mg/L were dosed into synthetic wastewater and daily BOD of each Ni(II) concentration was measured for a period of 20 days.

Based on the results obtained in this study, the following conclusions can be drawn:

1. In BOD determinations, microorganisms in BOD bottle, do not get acclimitized to Ni(II) at the concentrations tested.

2. Ni(II) is toxic to BOD and the degree of toxicity depends on the level of Ni(II) in the wastewater.

3. In this study, it was aimed, the comparison of Thomas method and the model proposed by Swamee and Ojha for the BOD exertion in the presence of Ni(II) and this study revealed that, the BOD exertion in the presence of Ni(II) can be described by a new model proposed by Swamee and Ojha much more satisfactorily.

4. Fifth day BOD exertion is about 50% of the twentieth day BOD exertion for all Ni(II) concentrations tested. This may be concluded as the validity of the same rate expression for all Ni(II) concentrations.

5. Although it is expected to have a lag phase in BOD exertion in the presence of Ni(II), BOD exertion started immediately and continue by following the same rate expression.

6. From the application of Swamee and Ojha'S model to experimental results; decreasing reaction rate constants, m_c with increasing Ni(II) concentrations were observed. Contradictory to this, by Thomas method, increasing reaction rates were observed with increasing Ni(II) concentrations.

CHAPTER VII

RECOMMENDATIONS

Recommendations for further research on the subject can be summarized as:

1. Research on the effects of heavy metals on BOD exertion kinetics should be completed for heavy metals other than Ni(II).

2. The effect of Ni(II) for concentrations more than 10.0 mg/L on the BOD exertion kinetics should be studied to have better insight about the stimulation caused by Ni(II).

3. Effect of suspended solid concentration on the effect of Ni(II) on BOD exertion should be studied.

4. The combined effects of Ni(II) and other heavy metals should be investigated.

5. Other methods used to determine BOD parameters, k and L such as moment method, least square method etc., should also be used in the evaluation of k and L in order to make more reliable comparison.

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APPENDICES

APPENDIX A

BIOCHEMICAL OXYGEN DEMAND DETERMINATION BY WINKLER METHOD

APPARATUS

a.Incubation bottles, 250-300 ml capacity, with ground-glass stoppers: Bottles should be cleaned with a good detergent and thorougly rinsed and draine before use. As a precaution agai-nist drawing air into the dilution bottle during incubation, a water seal is recommended. Satisfactory water seals are obta-ined by inverting the bottles in a water bath or adding water to the flared mouth of special BOD bottles.

b. Air incubator or water bath, thermostatically controlled at 20°C ± 1C: All light should be excluded to prevent formation of DO by algea in the sample.

REAGENTS

a. Distilled water: Water used for solutions and for prepara-tion of dilution water must be of the highest quality, distil-led from a block tin or all-glass still; it must contain less than 0.01 mg/L copper and be free of chlorine, chloramines, caustic alkalinity, organic material or acids.

b. Phosphate buffer solution: Dissolve 8.5 g potassium dihyd-rogen phosphate, KH_2PO_4, 21.75 g dipotassium hydrogen phosphate; KH_2PO_4, 33.4 g disodium hydrogen phosphateheptahydrate, $Na_2HPO_4.7H_2O$, and 1.7 g ammonium chloride, NH_4Cl, in about 500 ml distilled water and dilute to 1 liter. The pH of this buffer should be 7.2 without further adjustment. Discard the reagent if there is any sign of biological growth in the stock bottle.

c. Magnesium sulfate solution: Dissolve 22.5 g $MgSO_4.7H_2O$ in distilled water and dilute to 1 liter.

d. Calcium chloride solution: Dissolve 22.5 g anhydrous $CaCl_2$ in distilled water and dilute to 1 liter.

e. Ferric chloride solution: Dissolve 0.25 g $FeCl_3.6H_2O$ in distilled water and dilute to 1 liter.

f. Acid and alkali solutions, 1N: For neutralization of waste samples which are either caustic or acidic.

g. Sodium sulfite solution, 0.025N: Dissolve 1.575 g anhydrous Na_2SO_4 in 1,000 ml distilled water. This solution is not stable and should be prepared daily.

h. Seeding: The purpose of seeding is to introduce into the sample a biological population capable of oxidizing the organic matter in the wastewater. Where such microorganisms are already present, as in domestic sewage or unchlorinated effluents and surface waters, seeding is unnecessary and should not be employed.

When there is reason to believe that the sample contains very few organisms the dilution should be seeded. The standard seed material is settled domestic sewage which has been stored at 20C for 24-36 hr. The standard seed concentration is 1-2 ml per liter of dilution water.

Some samples-for example, certain industrial wastes-may require seeding because of low microbial population, but they contain organic compounds which are not readily amenable to oxidation by domestic sewage seed. For evaluating the effect of such a waste in a treatment system, more meaningful results may sometimes be realized by the use of specialized seed material containing organisms adapted to the use of the organic compounds present. Such adapted seed is best obtained from the effluent of a biological treatment process receiving the waste in question, or from the receiving water below the point of discharge if the waste is not being treated. When these sources are not available, adapted seed may be developed in the laboratory by continuously aerating a large sample of water and feeding it with small daily increments of the particular waste, together with soil or domestic sewage, until a satisfactory microbial population has developed. The special circumstances which call for the use of adapted seed may also require use of a seed concentration higher than the standard 1-2 ml/L. The kind and amount of seed required for such special-purpose studies must be decided on the basis of prior experience with the particular waste and purpose for which the determination is being performed.

Adapted seed has also been used when attempting to estimate the effect of a waste on the receiving water. However, refer to the introduction to this method in this connection (Section 219.1).

PROCEDURE

1. Preparation of Dilution Water: Before use, store the distilled water in cotton-plugged bottles long enough to permit it to become saturated with DO; or, if such storage is not practical, saturate the water by shaking the partially filled bottle or by aerating with a supply of clean compressed air. The distilled water should be at 20±1°C.

Place the desired volume of distilled water in suitable bottle and add 1 ml each of phosphate buffer, magnesium sulfate, calcium chloride and ferric chloride solutions for each liter of water. If dilution water is to be stored in the incubator, add the phosphate buffer just prior to using the dilution water.

2. Seeding: If the dilution water is seeded, it should be used the same day it is prepared.

3. Dilution Technique: Make several dilutions of the prepared sample so as to obtain the required depletions. The following dilutions are suggested: 0.1-1.0% for strong trade wastes, 1-5% for raw and settled sewage, 5-25% for oxidized effluents, and 25-100% for polluted rivers.

(i) Carefully siphon standard dilution water, seeded if necessary, into a graduated cylinder of 1,000-2,000 ml capacity, filling the cylinder half full without the entrainment of air. Add the quantity of carefully mixed sample to make the desired dilution and dilute to the appropriate level with dilutin water. Mix well with a plunger type mixing rod, avoiding entrainment of air. Siphon the mixed dilution into two BOD bottles, one for incubation and the other for determination of initial DO in the mixture; stopper tightly and incubate for 5 days at 20C. The BOD bottles should be water-sealed by inversion in a tray of water in the incubator or by use of a special water-seal bottle. Prepare succeeding dilutions of lower concentration in the same manner or by adding dilution water to the unused portion of preceeding dilution.

(ii) The dilution technique may be greatly simplified when suitable amounts of samplr are measured directly into bottles of known capacity with a large-tip volumetric pipet and the bottle is filled with sufficient dilution water that the stopper would be inserted without leaving air bubbles. Dilutions greater than 1:100 should be made by diluting the waste in a volumetric flask before it is added to the incubation bottles for final dilution.

4. Determination of DO: If the sample represents 1% or more of the lowest BOD dilution, determine DO on the undiluted sample. This determination is usually omitted on sewage and settled effluents known to have DO content of practically zero. With samples having an immediate oxygen demand, a calculated initial DO should be used, in as much as a demand represents a load on the receiving water.

5. Incubation: Incubate the blank dilution water and the diluted samples for 5 days in the dark at 20C. Then determine the DO in the incubated samples and the blank, using the azide modification of the iodometric method or a membrane electrode. Unless the electron membrane is used, the alum flocculation method is recommended for incubated samples of muds, and the copper sulfate-sulfamic acid method for activated sludges. In special cases, other modifications may be necessary. Those dilutions showing a residual DO of at least 1mg/L and a depletion of at least 2mg/L should be considered the most reliable.

6. Seed Correction: If the dilution water is seeded, determine the oxygen depletion of the seed by setting up a separate se-

ries of seed dilutions and selecting those resulting in 40-70 % oxygen depletions in 5 days. One of these depletions is then used to calculate the correction due to the small amount of seed in the dilution water. Do not use seeded blank for seed correction because the 5 day seeded dilution water blank is subject to erratic oxidation due to the very high dilution of seed, which is not characteristic of the seeded sample.

6. Precision and accuracy: There is no standard against which the accuracy of the BOD test can be measured. To obtain precision data, a glucose-glutamic acid mixture was analyzed by 34 laboratories, with each laboratory using its own seed material. The geometric mean of all results was 184 mg/L and the standard deviation of that mean was ± 31 mg/L. The precision obtained by a single analyst in his own laboratory was ±11 mg/L at a BOD of 218 mg/L.

APPENDIX B

BOD EXERTION MODEL PROPOSED BY BERKÜN (1974)

Thr following equations obtained from the first order equations can be used for the calculation of k values. Ultimate BOD values can also be calculated from these equations.

$$C = \Sigma_1^n y_i$$

$$C_1 = y_1 + 2y_2 + \ldots\ldots\ldots\ldots + ny_n$$

$$C_2 = n - \frac{y_2 - y_1}{y_1} - \frac{y_3 - y_2}{y_1} - \ldots\ldots\ldots - \frac{y_n - y_{n-1}}{y_1}$$

$$C_3 = (1 + 2 + 3 + \ldots\ldots + n) - \frac{y_2 - y_1}{y_1} - \frac{2(y_3 - y_2)}{y_1} - \ldots\ldots\ldots - \frac{(n-1)(y_n - y_{n-1})}{y_1}$$

$$\frac{C}{C_1} = \frac{C_2 - e^{-nk}}{C_3 - ne^{-nk}}$$

$$e^{-nk} = \frac{C_1 C_2 - CC_3}{C_1 - nC}$$

$$k = \frac{1}{n} \ln\left[\frac{C_1 - nC}{C_1 C_2 - CC_3}\right]$$

$$L = \frac{\Sigma y}{n - \Sigma e^{-kt}}$$

where;

y : observed BOD values

n : number of observations

APPENDIX C

RESULTS OF FIRST SET OF EXPERIMENTS

Table C1. Results of First Set of Experiments

Time (day)	no-Ni(II) case	1mg/l Ni(II) conc. I	1mg/l Ni(II) conc. II	2mg/l Ni(II) conc. I	2mg/l Ni(II) conc. II	3mg/l Ni(II) conc. I	3mg/l Ni(II) conc. II	4mg/L Ni(II) conc.	5mg/l Ni(II) conc. I	5mg/l Ni(II) conc. II	10mg/l Ni(II) conc. I	10mg/l Ni(II) conc. II
0	0	0	0	0	0	0	2.5	0	0	0	0	0
1	5	2.5	2.5	2.5	2.5	0	0	0	0	0	0	0
2	5	2.5	2.5	7.5	7.5	0	0	2.5	0	0	0	0
3	5	5	5	12.5	12.5	5	7.5	5	17.5	25	15	15
4	10	5	5	15	15	5	7.5		10	12.5	5	10
5	10	5	7.5	7.5	7.5	7.5	7.5	5	10	10	10	10
6	12.5	2.5	2.5	7.5	7.5	17.5	20	2.5	12.5	10	10	7.5
7	12.5	10	10	15	15	7.5	7.5	7.5	15	17.5	15	10
8	10	5	5	16	16	5	5	7.5				
9	12.5	5	5	11.5	18	2.5	2.5	10	2.5	7.5	5	5
10	15	10	10	19.25	21	2.5	5	15	12.5	10	15	12.5
11				21.25	23.75	10	12.5		12.5	17.5	12.5	10
12	10	7.5	7.5	21.25	23.75	17.5	20	0	20	15	12.5	12.5
13	35	7.5	7.5					5	10	20	12.5	12.5
14						10	12.5		15	20	17.5	12.5
15	10	10	7.5					7.5	20	17.5	15	15
16	47.5	7.5	7.5			12.5	10	5	20	17.5	12.5	12.5
17		5	5	14.1	16	15	12.5	7.5	20	20	15	15
18				23.75	26	15	12.5		20	17.5	15	15
19		15	10			12.5	7.5	7.5	12.5	10	12.5	12.5
20	50	15	15	21.25	21.25	10	12.5	7.5	20	20	17.5	17.5

APPENDIX D

RESULTS OF SECOND SET OF EXPERIMENTS

Table D1. Results of Second Set of Experiments

Time (day)	no-Ni(II) case		1mg/l Ni(II) conc.		2mg/l Ni(II) conc.		3mg/l Ni(II) conc.		4mg/L Ni(II) conc.	5mg/l Ni(II) conc.		10mg/l Ni(II) conc.	
	I	II	I	II	I	II	I	II		I	II	I	II
0	0	0	2.5	2.5	2.5	2.5	0	0	0	0	0	0	0
5	42.5	35	25	25	25	25	20	20	15	20	22.5	22.5	22.5
20	97.5	97.5	22.5	22.5	27.5	27.5	35	30	22.5	17.5	17.5	15	20

APPENDIX E

COMBINATION OF FIRST AND SECOND SETS OF EXPERIMENTS DATA

Table E1. Combination of First and Second Sets of Experiments Data(no-nickel case)

Time (day)	BOD value (mg/L)
0	0
1	5
2	5
3	5
4	10
5	10
6	12.5
7	12.5
8	10
9	12.5
10	15
12	10
13	35
15	10
16	47.5
20	50

Table E2. BOD Exertion of the Wastewater Bearing 1.0 mg/L Ni(II) Concentration
(Combination of First and Second Sets of Experiments)

Time (day)	BOD value (mg/L)
0	0
1	2.5
2	2.5
3	5
4	5
5	5
6	2.5
7	10
8	5
9	5
10	10
12	7.5
13	7.5
15	10
16	10
17	7.5
19	5
20	15

Table E3. BOD Exertion of the Wastewater Bearing 2.0 mg/L Ni(II) Concentration

(Combination of First and Second Sets of Experiments)

Time(day)	BOD value(mg/L)
0	0
1	2.5
2	7.5
3	12.5
4	15
5	7.5
6	7.5
7	15
8	16
9	13
10	20
11	21.25
12	21.25
17	15
18	23.75
20	25

Table E4. BOD Exertion of the Wastewater Bearing 3.0 mg/L Ni(II) Concentration
(Combination of First and Second Sets of Experiments)

Time(day)	BOD value(mg/L)
0	0
1	0
2	0
3	7.5
4	7.5
5	20
6	20
11	12.5
12	20
14	12.5
16	12.5
17	15
18	15
19	12.5
20	36

Table E5. BOD Exertion of the Wastewater Bearing 4.0 mg/L Ni(II) Concentration
(Combination of First and Second Sets of Experiments)

Time(day)	BOD value(mg/L)
0	0
1	0
2	2.5
3	5
5	5
7	7.5
8	7.5
9	10
10	15
20	22.5

Table E6. BOD Exertion of the Wastewater Bearing 5.0 mg/L Ni(II) Concentration (Combination of First and Second Sets of Experiments)

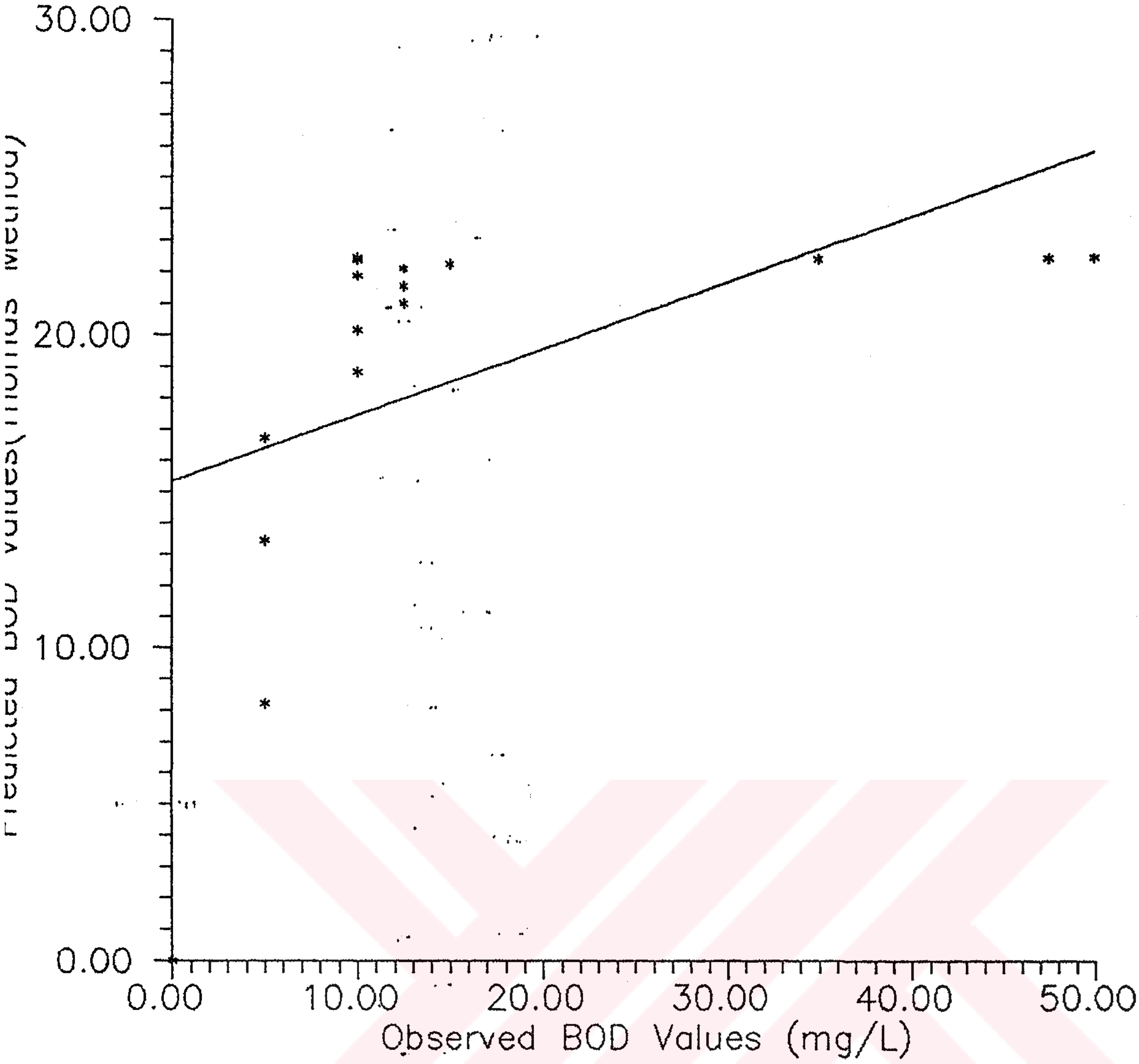
Time(day)	BOD value(mg/L)
0	0
1	0
2	0
3	21.25
4	12.5
5	10
6	12.5
7	17.5
9	7.5
10	12.5
11	17.5
12	20
13	20
14	20
15	20
16	20
17	20
18	20
20	20

Table E7. BOD Exertion of the Wastewater Bearing 10.0 mg/L Ni(II) Concentration (Combination of First and Second Sets of Experiments)

Time(day)	BOD value(mg/L)
0	0
1	0
2	0
4	7.5
5	10
6	10
7	12.5
10	13.75
11	12.5
12	12.5
13	12.5
14	15
15	15
16	12.5
17	15
18	15
19	12.5
20	17.5

APPENDIX F

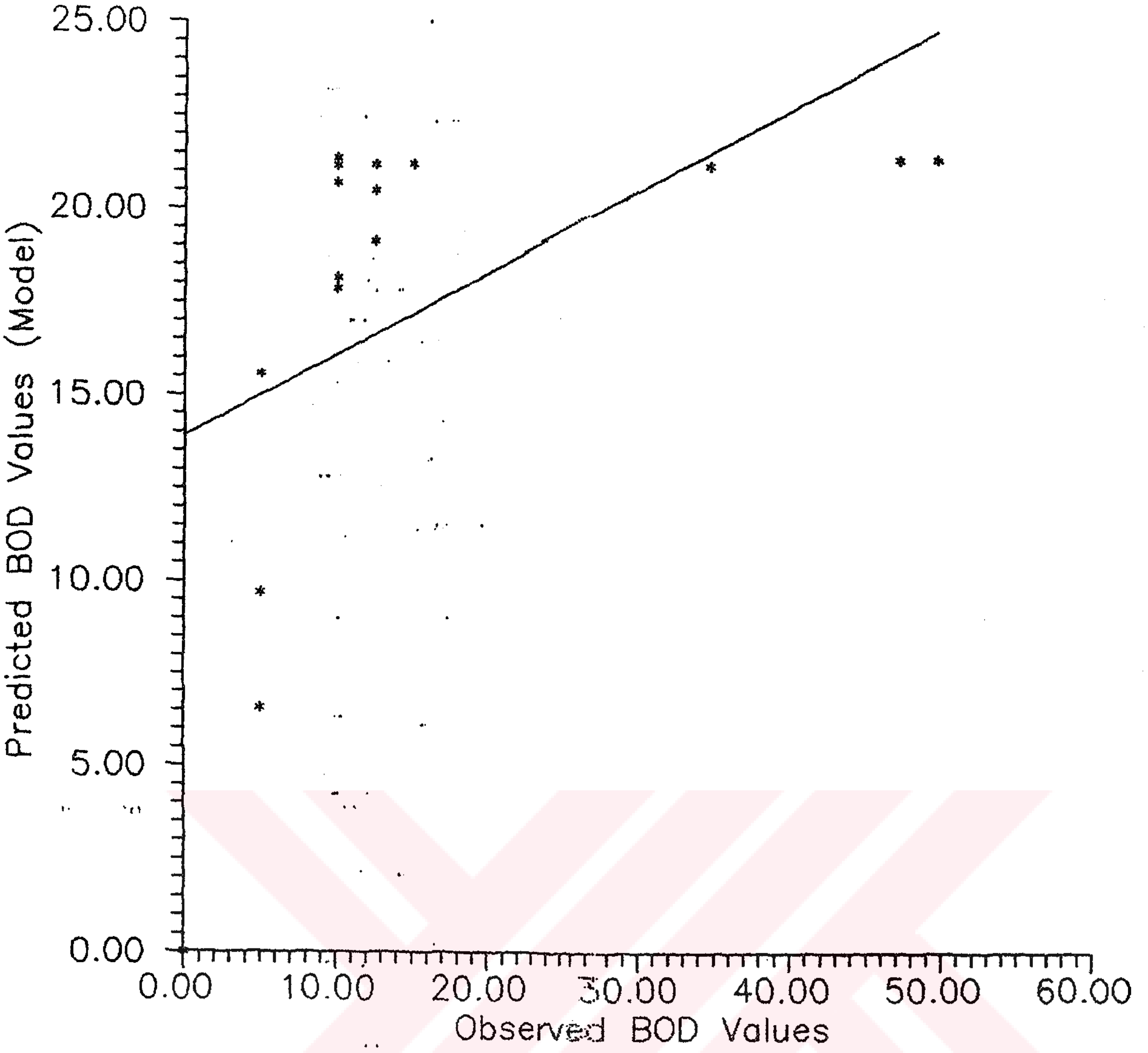
COMPARISON OF OBSERVED BOD EXERTION WITH THOMAS METHOD AND THE SWAMEE AND OJHA MODEL



y = 0.210269x + 15.3458

Correlation Coefficient: 0.68

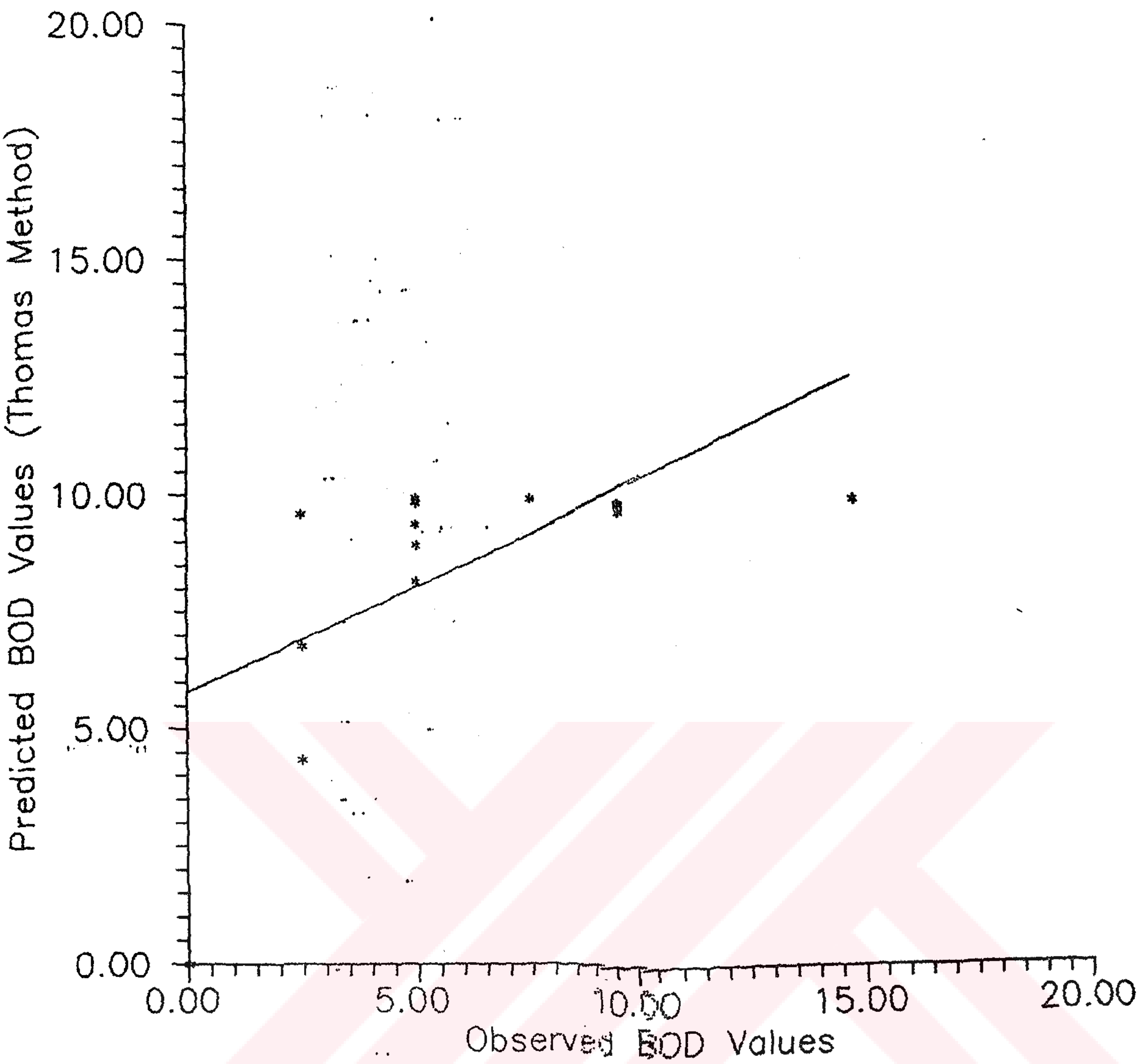
Figure F.1. Observed BOD Values vs Predicted BOD Values by Thomas Method (for 0.0 mg/L Ni(II).........101



y = 0.217505x + 13.9009

Correlation Coefficient: 0.85

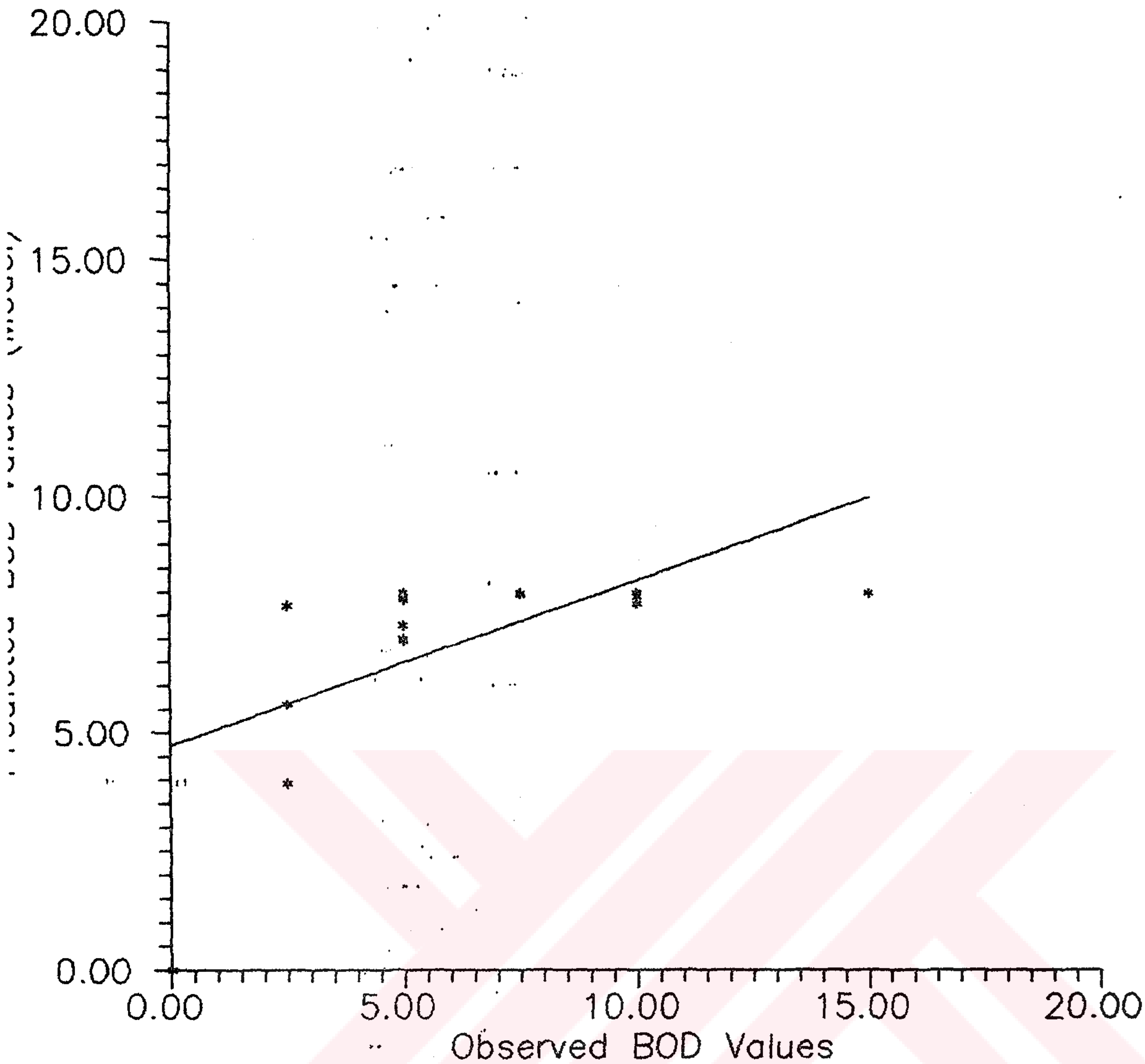
Figure F.2. Observed BOD Values vs Predicted BOD Values by Swamee and Ojha Model(for 0.0 mg/L Ni(II))



y = 0.450841x + 5.77796

Correlation Coefficient: 0.72

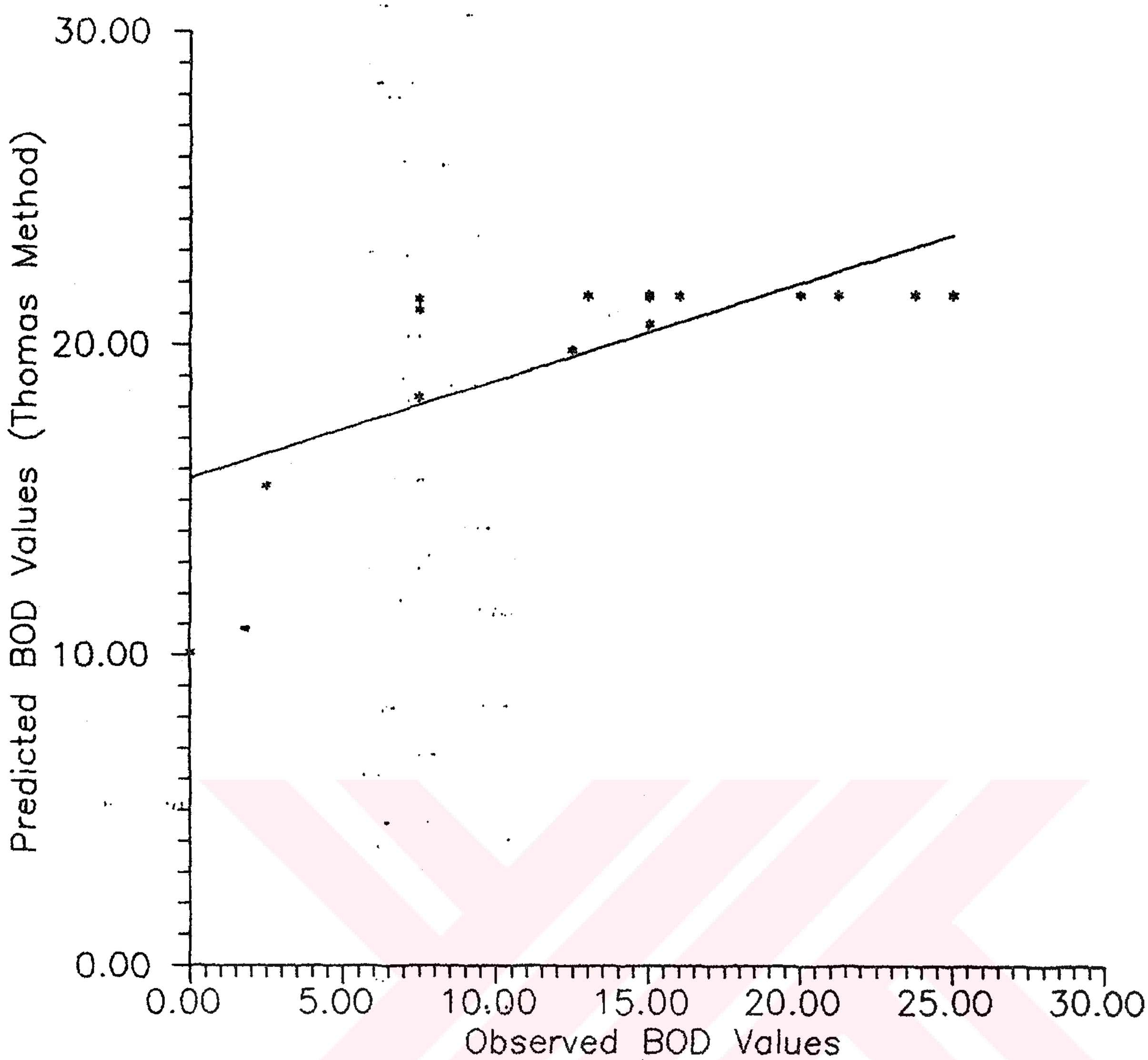
Figure F.3. Observed BOD Values vs Predicted BOD Values by Thomas Method (for 1.0 mg/L Ni(II))



$y = 0.350707x + 4.73104$

Correlation Coefficient: 0.85

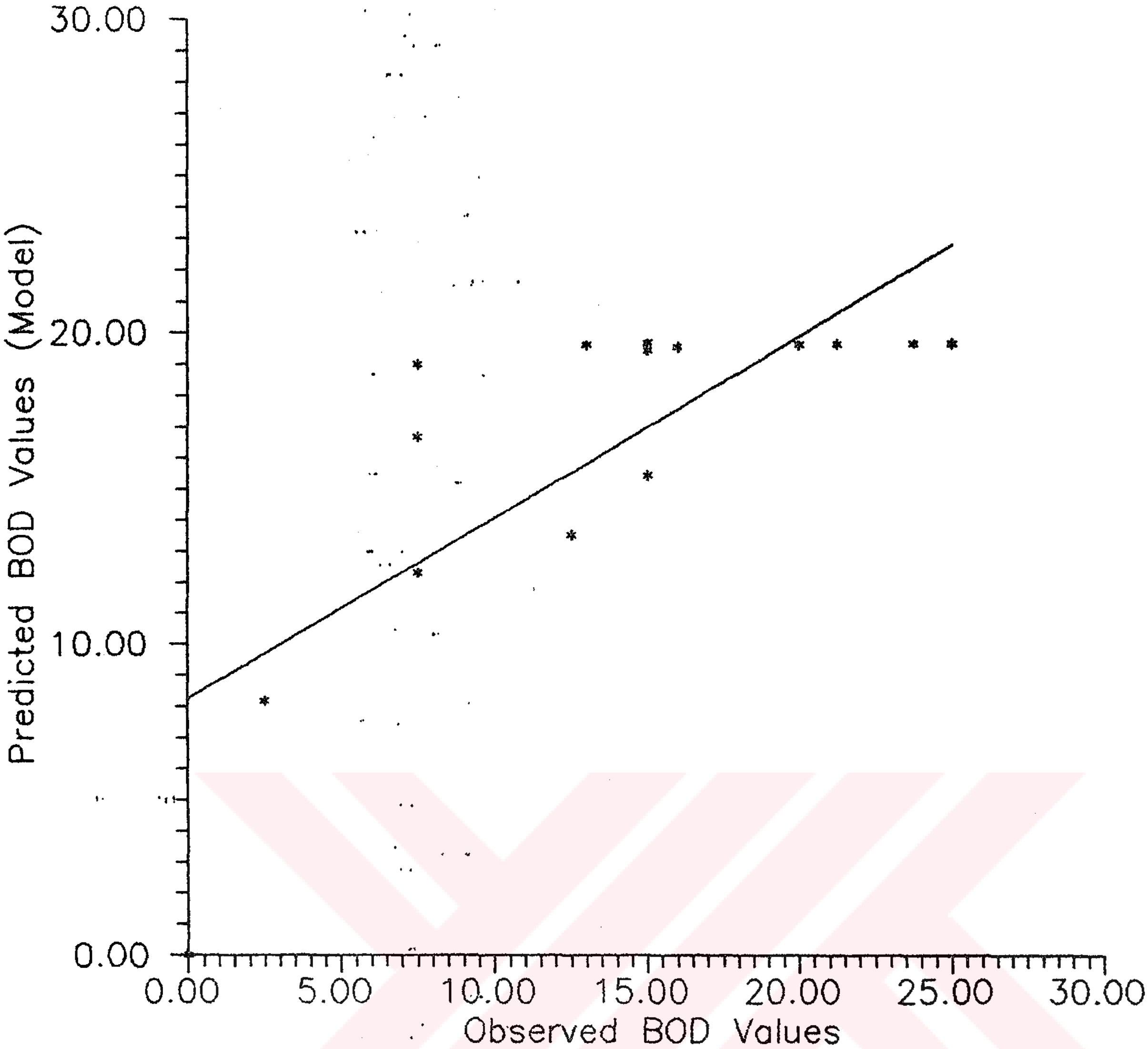
Figure F.4. Observed BOD Values vs Predicted BOD Values by Swamee and Ojha Model(for 1.0 mg/L Ni(II))



y = 0.312534x + 15.7228

Correlation Coefficient: 0.47

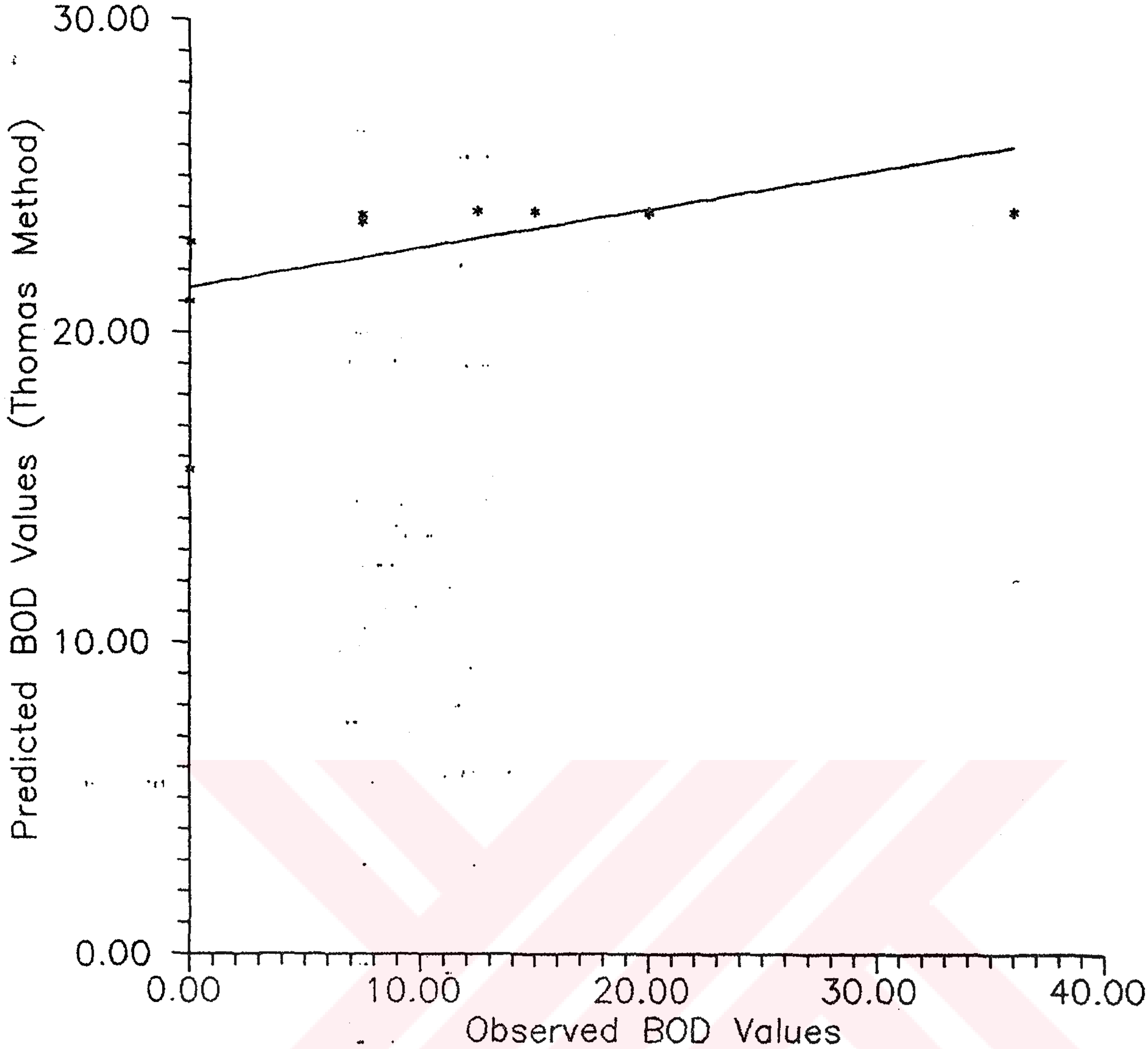
Figure F.5. Observed BOD Values vs Predicted BOD Values by Thomas Method (for 2.0 mg/L Ni(II))



y = 0.583694x + 8.23676

Correlation Coefficient: 0.68

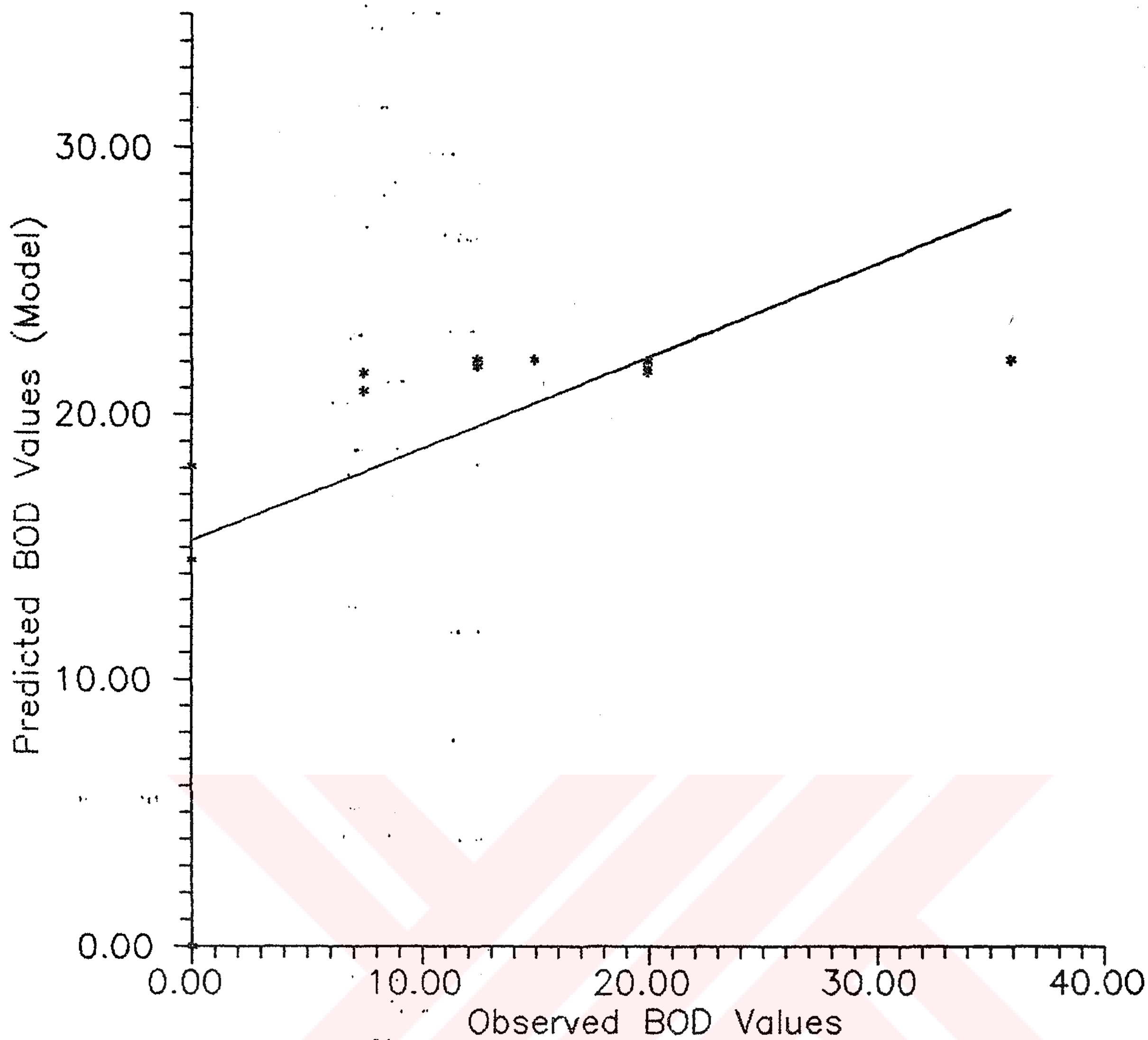
Figure F.6. Observed BOD Values vs Predicted BOD Values by Swamee and Ojha Model(for 2.0 mg/L Ni(II))



y = 0.125461x + 21.4379

Correlation Coefficient: 0.63

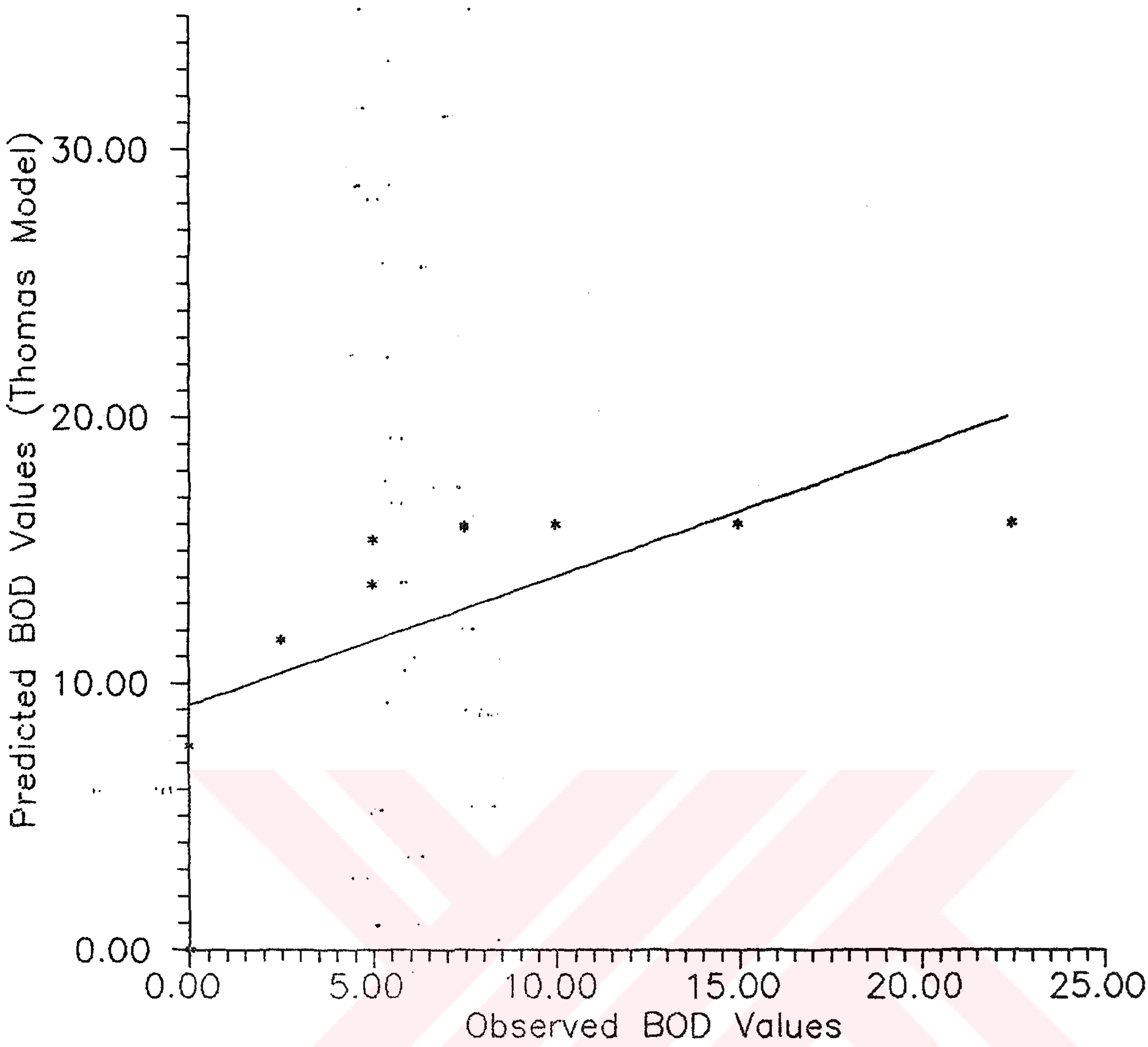
Figure F.7. Observed BOD Values vs Predicted BOD Values by Thomas Method (for 3.0 mg/L Ni(II))



y = 0.345168x + 15.255

Correlation Coefficient: 0.81

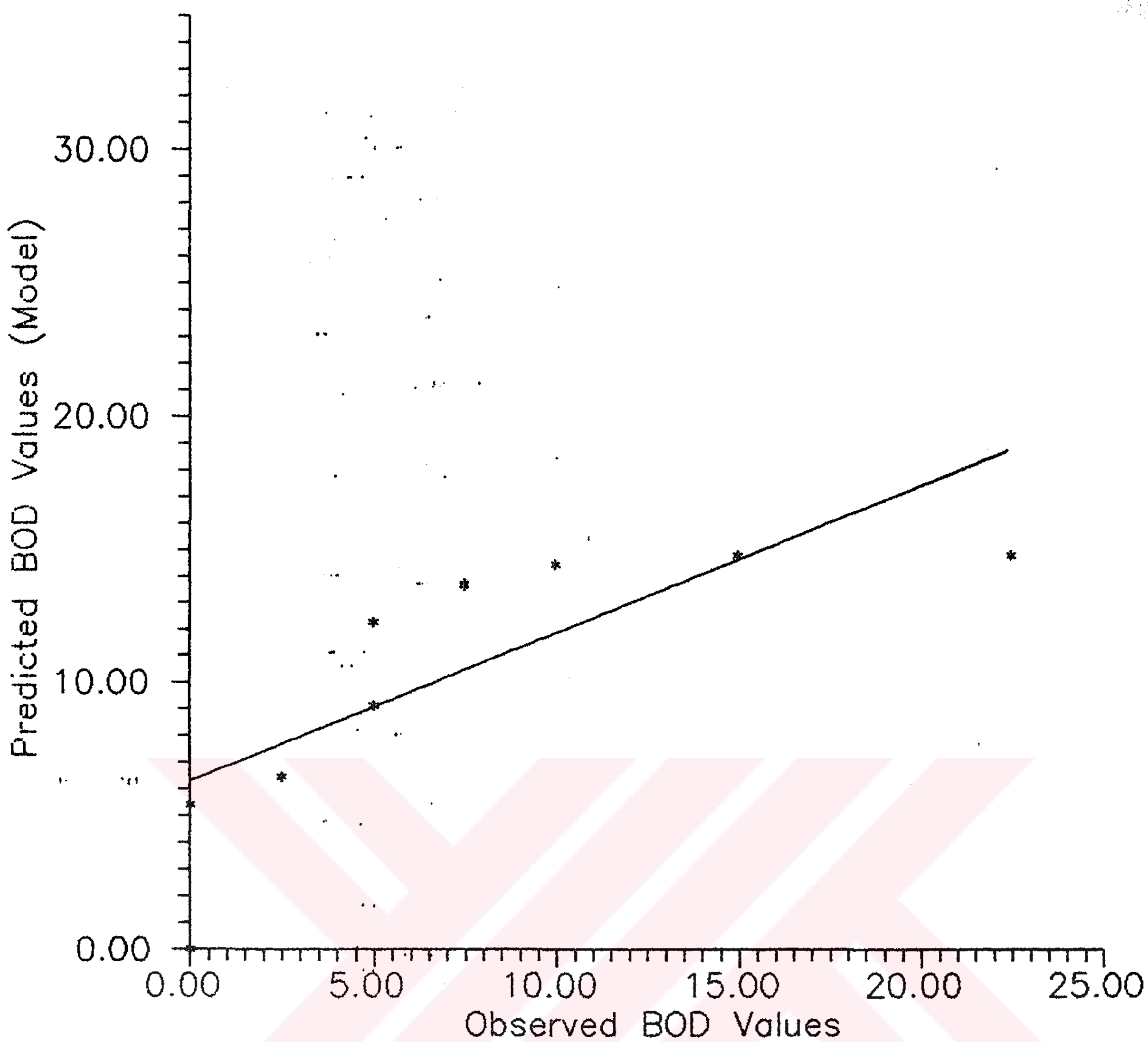
Figure F.8. Observed BOD Values vs Predicted BOD Values by Swamee and Ojha Model(for 3.0 mg/L Ni(II))



y = 0.485371x + 6.31014

Correlation Coefficient: 0.69

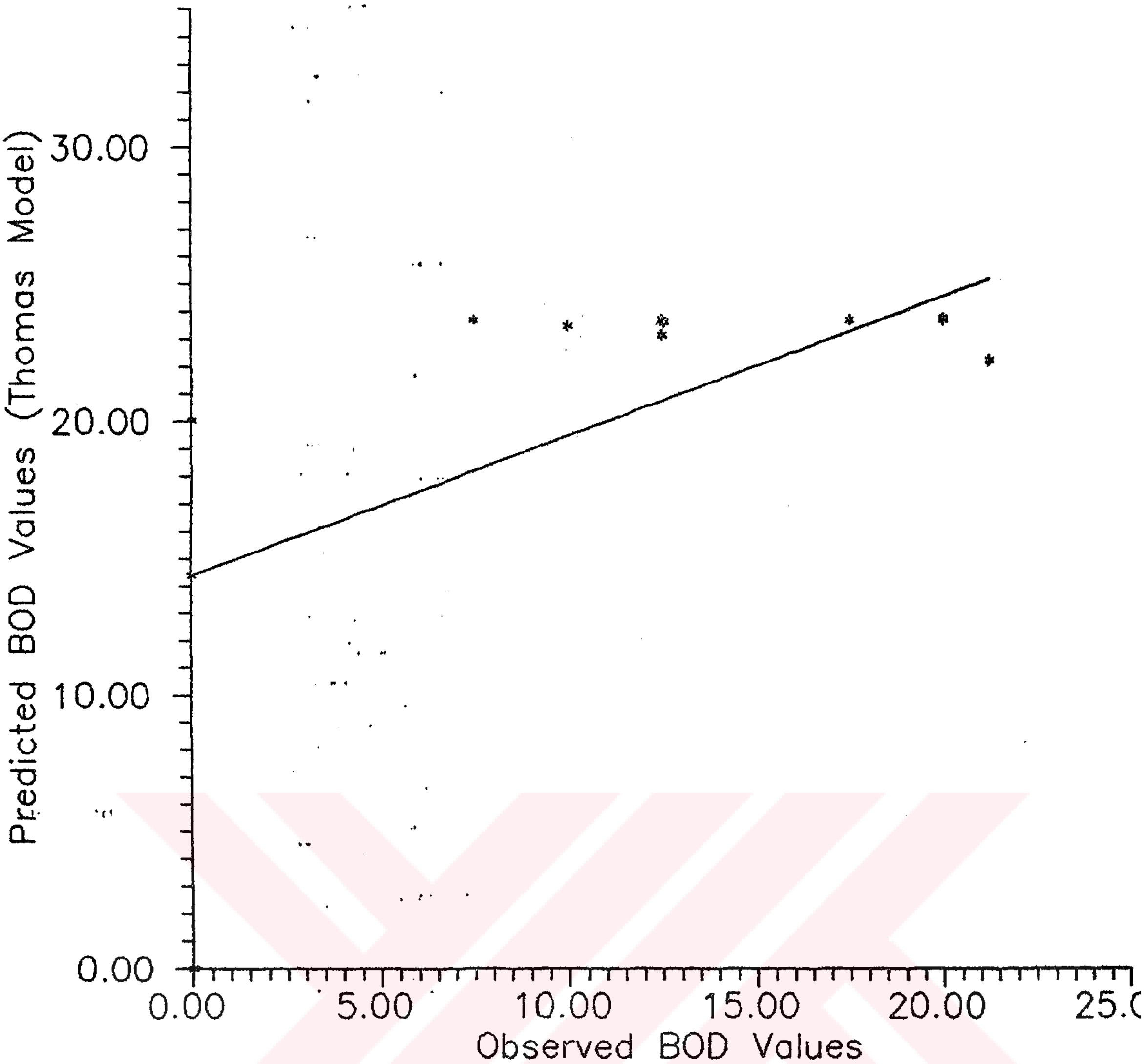
Figure F.7. Observed BOD Values vs Predicted BOD Values by Thomas Method (for 4.0 mg/L Ni(II))



y = 0.554514 + 9.18971

Correlation Coefficient: 0.79

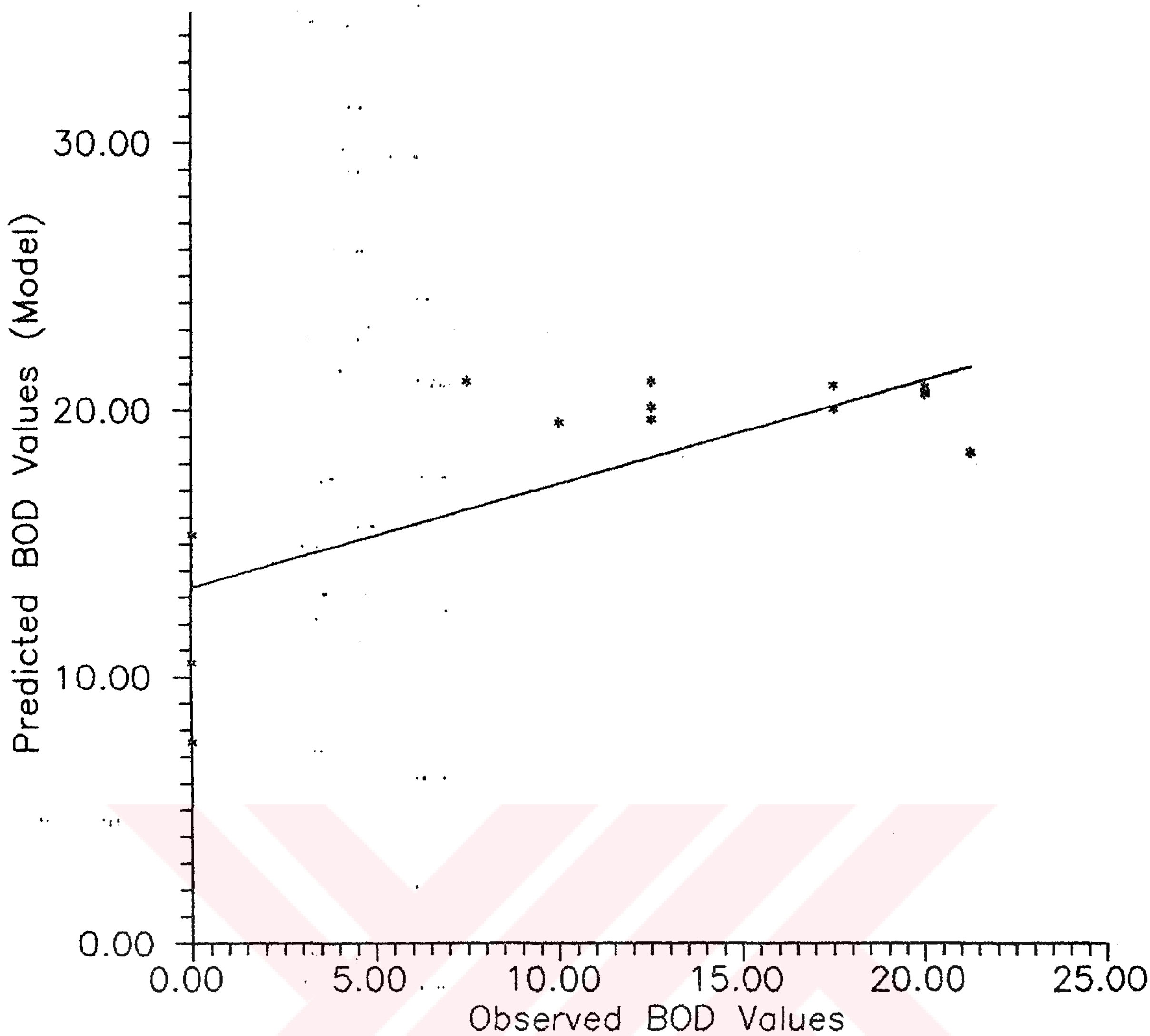
Figure F.10.Observed BOD Values vs Predicted BOD Values by Swamee and Ojha Model(for 4.0 mg/L Ni(II))



y = 0.50762x + 14.4063

Correlation Coefficient: 0.56

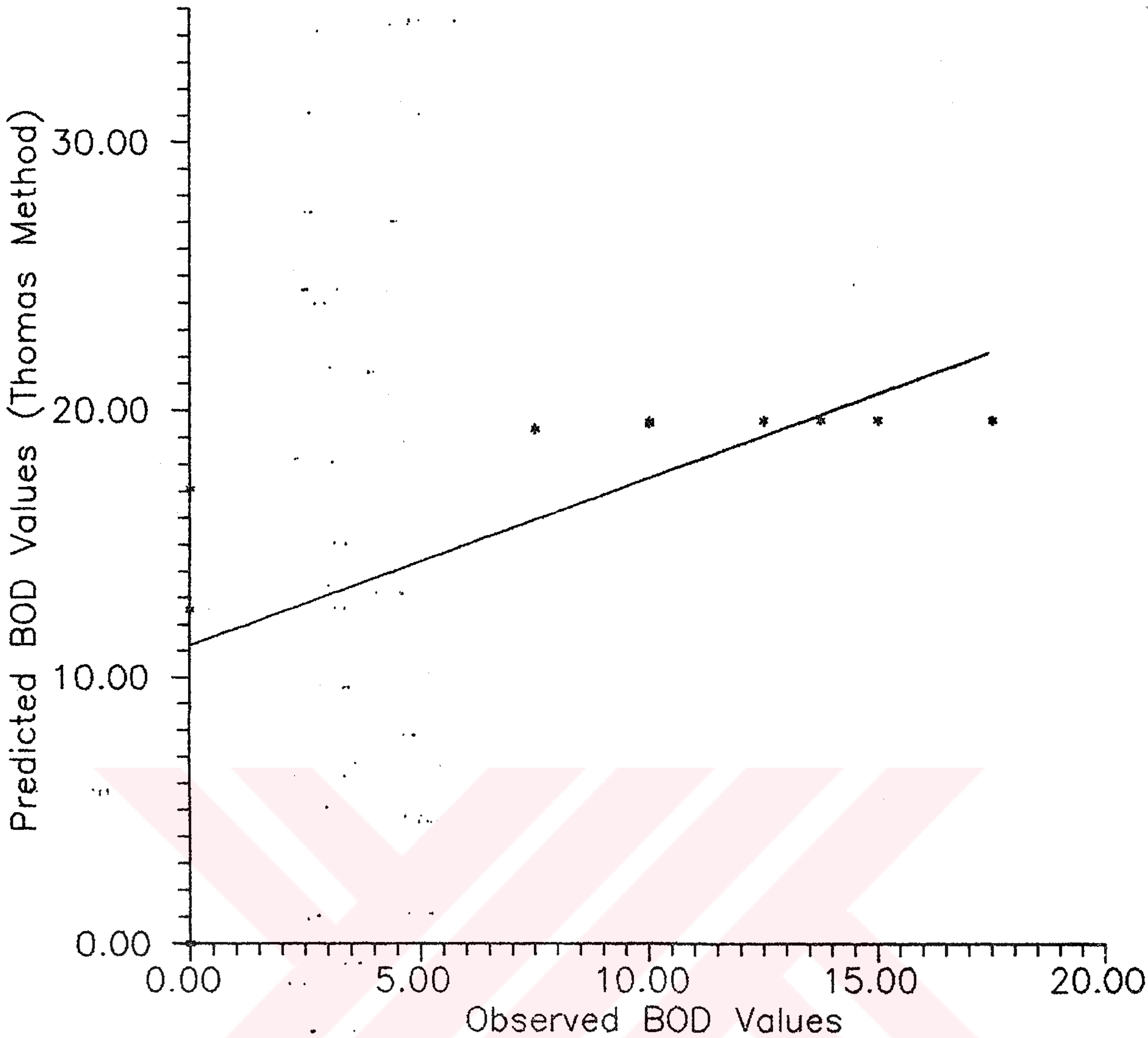
Figure F.11.Observed BOD Values vs Predicted BOD Values by Thomas Method (for 5.0 mg/L Ni(II))



y = 0.554514 + 9.18971

Correlation Coefficient: 0.79

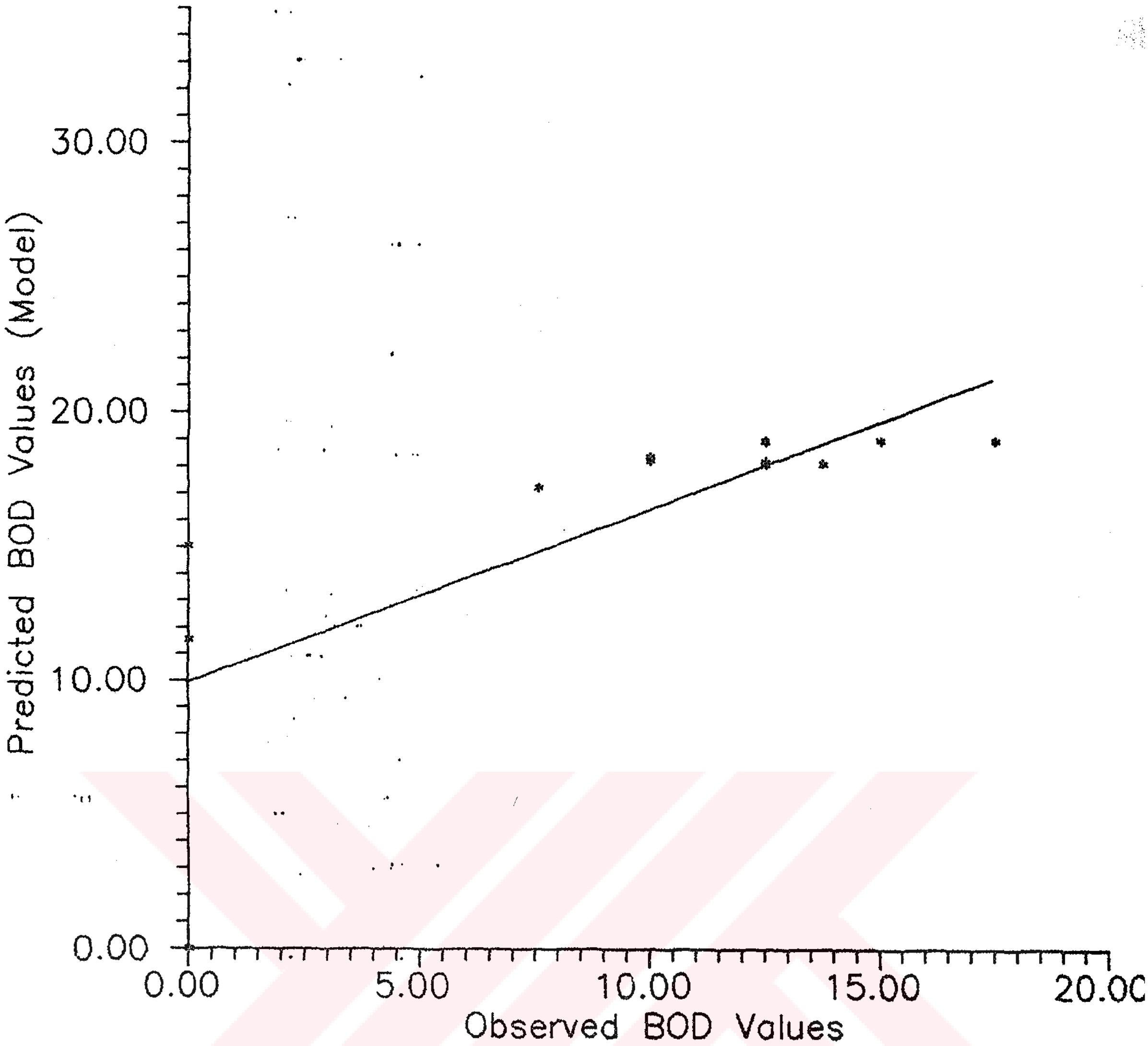
Figure F.12.Observed BOD Values vs Predicted BOD Values by Swamee and Ojha Model(for 5.0 mg/L Ni(II))



y = 0.627977x + 11.2261

Correlation Coefficient: 0.74

Figure F.13.Observed BOD Values vs Predicted BOD Values by Thomas Method (for 10.0 mg/L Ni(II))



y = 0.649585 + 9.93966

Correlation Coefficient: 0.92

Figure F.14.Observed BOD Values vs Predicted BOD Values by Swamee and Ojha Model(for 10.0 mg/L Ni(II))