T.R.
VAN YUZUNCU YIL UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF CHIEMICAL ENGINEERING

OPTIMIZATION OF TOLUIDINE BLUE BIOSORPTION CONDITIONS FROM AQUEOUS SOLUTIONS BY [POLYPORUS SQUAMOSUS] FUNGI AS ABSORBENT WITH RESPONSE SURFACE METHODOLOGY

M.Sc. THESIS

PREPARED BY: Liqaa Samir ESMAIL
SUPERVISOR: Assist. Prof. Dr. Duygu ALPASLAN

VAN-2018

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KABUL VE ONAY SAYFASI

Kimya Mühendisliği Anabilim Dalı'nda Dr. Öğr. Duygu Alpaslan danışmanlığında, Likaa Samir İSMAİL tarafından sunulan "OPTIMIZATION OF TOLUIDINE BLUE BIOSORPTION CONDITIONS FROM AQUEOUS SOLUTIONS BY [*Polyporus squamosus*] FUNGI AS ABSORBENT WITH RESPONSE SURFACE METHODOLOGY" isimli bu çalışma Lisansüstü Eğitim–Öğretim Yönetmeliği'nin ilgili hükümleri gereğince 22/06/2018 tarihinde aşağıdaki jüri tarafından oy birliği ile başarılı bulunmuş ve Yüksek Lisans Tezi olarak kabul edilmiştir.

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ACCEPTANCE and APPROVAL PAGE

This thesis entitled "OPTIMIZATION OF TOLUIDINE BLUE BIOSORPTION CONDITIONS FROM AQUEOUS SOLUTIONS BY [*Polyporus squamosus*] FUNGI AS ABSORBENT WITH RESPONSE SURFACE METHODOLOGY" presented by Likaa Samir İSMAİL under supervision of Asst. Prof. Duygu ALPASLAN in the department of Chemical Engineering has been accepted as a M. Sc. thesis according to Legislations of Graduate Higher Education on 22/06/2018 with unanimity of the members of jury.

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Member: Asst. Prof. Duygu ALPASLAN   Signature:

This thesis has been approved by the committee of The Institute of Natural and Applied Science on 02../..7..../2018. with decision number 2018-30/1

Signature

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THESIS STATEMENT

All information presented in the thesis obtained in the frame of ethical behavior and academic rules. In addition, all kinds of information that does not belong to me have been cited appropriately in the thesis prepared by the thesis writing rules.

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ABSTRACT

OPTIMIZATION OF TOLUIDINE BLUE BIOSORPTION CONDITIONS FROM AQUEOUS SOLUTIONS BY [POLYPORUS SQUAMOSUS] FUNGI AS ABSORBENT WITH RESPONSE SURFACE METHODOLOGY

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M.Sc. Thesis, Chemical Engineering Department
Supervisor: Assist. Prof. Dr.Duygu ALPASLAN
June 2018, 73 pages

Textile wastewater including large amount of dyes and heavy metals can have adverse impacts on human health and surface water. In this work, biosorption Toluidine Blue from aqueous media onto natural *Polypourus Squamosus* fungi as a low-cost biosorbent was investigated. Central Composite Design (CCD) in Response Surface Methodology (RSM) was successfully applied to optimize the biosorption condition. Medium parameters affected the biosorption of Toluidine Blue were determined to be initial pH, initial Toluidine Blue (Tb) concentration, temperature, and absorbent dosage. All experiments were carried out in a batch system using 250 ml flasks containing 100 ml of Toluidine Blue solution with a temperature controlled magnetic stirrer. The Tb concentrations remaining in filtration solutions after biosorption were analysed using UV-Spectro. With the obtained quadratic model, the optimal conditions for maximum biosorbed Toluidine blue were calculated to be 7, 27.5mg/L, 35°C and 0.05g for pH, $C_{\circ}$, T ($^{\circ}$C) and adsorbent dosage, respectively. Furthermore, most known isotherem models such as Langmuir and Freundlich were computed to find best-fitted model.

Keywords: Biosorption, Toluidine blue, Optimization, *Polyporus Squamosus*, Response surface methodology

ÖZET

MESLEKİ YÜZEY METODOLOJİSİ İLE EMNİYETLİ OLARAK [POLYPORUS SQUAMOSUS] FUNGI TOLUİDİNDİR MAVİ BİYOORPİYON KOŞULLARININ OPTİMİZASYONU

ESMAIL Liqaa Samir
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Çok miktarda boya ve ağır metal içeren tekstil atıksularının insan sağlığı ve yüzey suyu üzerinde olumsuz etkileri olabilir. Bu çalışmada, Merkez Kompozit Tasarım (MKT) Yanıt Yüzey Metodolojisinde (YYM) Toluidin mavisinin biyosorpsiyonunda biyosorbent olarak doğal *Polyporus Squamosus* mantarları kullanılmıştır. Toluidin mavisinin sulu ortamdan yeni bir biyosorbent ile uzaklaştırılması gerçekleştirildi. Literatüre göre daha önce Toluidin Mavi'sinin biyosorbsiyonu için kullanılmamış olan doğal *Polyporus Squamosus* mantarı, düşük maliyetli bir biyosorbent olarak kullanılmış ve biyosorpsiyon koşulları, yanıt yüzey metodolojisi (YYM) ile analiz edilmiştir. Toluidin mavisinin biyosorpsiyonunu etkilemesi beklenen ortam parametrelerin başlangıç pH, başlangıç Toluidin mavi (Tm) konsantrasyonu ($C_{\circ}$), sıcaklık T ($^{\circ}$C) ve absorbent mikarı olduğu belirlenmiştir. Tüm deneyler, bir sıcaklık kontrollü manyetik karıştırıcı ile 100 ml Toluidin Mavi çözeltisi içeren 250 ml'lik şişeler kullanılarak bir parti sisteminde gerçekleştirilmiştir. Biyosorpsiyondan sonra filtrasyon çözeltilerinde kalan Tm konsantrasyonları, UV-Spectro kullanılarak analiz edildi. Elde edilen kuadratik model ile maksimum biyosorlu Toluidin mavisi için optimal koşullar sırasıyla pH, Concentartion, T ($^{\circ}$C) ve absorbant miktari için sırasıyla 7, 27.5 mg / L, 35°C ve 0.05 mg olarak hesaplanmıştır. Dahası, Tm absorpsiyonuna mekanizmasını bulmak için Langmuir ve Freundlich gibi bilinen izoterm modelleri hesaplanmıştır.

Anahtar kelimeler: Biyosorpsiyon, Toluidin mavisi, Optimizasyon, *Polyporus Squamosus*, Tepki yüzeyi metodolojisi

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LIST OF ABBREVIATIONS

Some abbreviations used in this study are present below, along with descriptions.

Symbol	Description
C_o	Initial concentration
%Wt	Weight percentage
°C	Celsius
K	Kelvin
Rpm	Rotation Per Minute
g	Gram
mg	Milligram
L	Liter
ml	Milliliter
m	Meter
mol	Mole
%	Percentage
NaOH	Sodium Hydroxide
S	Second
R^2	Regression stability index
HCl	Hydrochloric acid
Nm	Nanometer
V	Volume
H	Hour

Abbreviation	Description
ANOVA	Analysis of variance
BET	Bruner, Emmett and Teller method
CCD	Central Composite Design
TB	Toluidine Blue dye
WHO	World Health Organization
ppm	Part Per Million
RSM	Response Surface Methodology
PZC	Point of Zero Charge

1. INTRODUCTION

The pollution of water with organic pollutants is causing increasing environmental problems (Kumar and Min, 2011). Specifically, the organic pollutants are widely found in wastewater from industries such as dye mining, metal plating, and electronics. Although some organic compound used in dentistry, medicine and dye industrial coatings, is ubiquitous in the environment and derives from both natural sources and human activities (Zhang et al., 2005). The industrial textile wastewater, which contains high chemical and biological oxygen demand, suspended solids, different salts, surfactants, dyes, heavy metals, mineral oils, etc., is considered a pollutant to water resources (Kumar et al., 2014).

For decades, traditional separation methods including chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, and electrochemical processes have successfully been applied to the removal of organic pollutants from industrial effluents. However, technical and economic constraints encountered in the application of these traditional methods have shown the need to search for new technological solutions for the removal of organic compounds from waste streams. Most of these methods have several disadvantages and tend to very expensive and time-consuming. However, among these methods, adsorption and biosorption are generally considered simple, relatively inexpensive and effective methods of removing organic pollutants from wastewater (Ji et al., 2012; Holda, 2013; Wang et al., 2013). The use of microorganisms such as bacteria, fungi and yeast in treating wastewaters containing organic pollutants is gaining favor (Bhatti and Amin, 2013; Bhatti and Hamid, 2014; Hanif et al., 2015).

Fungal biosorption occurs because of ionic interactions and complex formation between metal ion or dyes and functional groups, which are present on fungal cell surfaces. These functional groups include phosphate, carboxyl, amine and amid groups (Kapoor and Viraraghavan, 1997; Yan and Viraraghavan, 2003).

The removal of pollutants from aqueous solutions is one of the most important issues in wastewater treatment plans. As absorption processes have high impact, providing high-quality water after treatment that can be recycled, the cost of the absorbent used can be kept low and these processes are considered feasible. Therefore, the absorption processes and the study of absorption kinetics in wastewater treatment are important to provide insights into the reaction pathways of the mechanism of absorption reactions (Ho and Mckay, 1999).

Wastewater contain both organic and inorganic chemicals consisting of dangerous compounds including dyes and surfactants, and also other contaminants such as dissolved and suspended solids, salts, dispersing agents, acids, alkalis, softeners, fixing agents, and other toxic compounds (Marechal et al., 2012). These dye wastes and contaminants can remain in the environment for a very long period if adequate treatment is not administered, and subsequently they become oncogenic and mutagenic through compositional changes (Kalaiarasi et al., 2012).

Toluidine blue was selected as the model contaminant because it is important industrial pollutant and has been observed to exert negative effects at very low concentrations.

In recent years, response surface methodology (RSM) has been widely used as a statistical method for rational experimental design and process optimization in the absence of mechanistic information, in contrast to traditional methods (Shahan et al., 2010). The reasons for its popularity are that it does not require additional consumption of chemicals for each parameter, nor is it especially time-consuming, costly or labor-intensive (Myers and Montgomery, 2002; Chi et al., 2012, Shahan and Ozturk, 2014; Ozturk and Shahan, 2015).

The other class of technologies is based on the biodegradability of dyes. Biological methods of dye degradation are regarded as most economically practical and eco-friendly method. Textile dye biodegradation can be achieved using several microorganisms, which include bacteria and fungi. Literature shows that wide varieties of microorganisms, including bacteria, algae and fungi, have good sorption ability for a number of pollutants (Walker et al., 2000). Among these microorganisms, fungi seem to be a good sorption material, because it can be produced economically using simple fermentation techniques and economic growth media. Fungi are also available as a by-product or waste material from various industrial processes (Fu et al., 2000). In the context of this study, *Polyporus squamosus* was selected to investigation the efficacy of fungi in the biosorption of Toluidine blue, which are commonly, used textile dyes.

This method is based on the fit of mathematical models (linear, square polynomial functions, and others) to the experimental results generated for the designed experiment and confirmation of the model obtained via statistical techniques. The major aim of this method is to vary all significant parameters simultaneously and then fit the experimental data to a mathematical model. That is, all the parameters studied for optimization vary at the same time. As a result, it can be said that required experiment number for optimization using RSM is less than the conventional methods.

Optimization via the RSM approach can be divided into six stages:

1- Selection of independent variables and possible responses.

2- Selection of the experimental design strategy.

3- Performing the experiments and obtaining the result.

4- Fitting the model equation to the experimental data.

5- Obtaining response graphs and verification of the model (ANOVA).

6- Determination of optimal conditions (Krowiak et al., 2014).

1.1. Background of the Study

There are more than 10,000 chemically different dyes that are being manufactured, while the world production of dye products and dye intermediates is about 7.108 kg annually (Toh et al., 2003). These dye products and dye intermediaries are mostly utilized by the textiles industries. Other industries making use of dye and dye products include pulp and paper industries, tanneries, pharmaceuticals industries, food packaging industries, paint and electroplating industries etc. Either wastes from these industries, which are mainly dye and dye intermediaries, can be liquid, gaseous or solid wastes, are highly colored, and are generated in vast amount (Parvathi et al., 2009). Large quantity of water is used during the dyeing process and washing of the textiles. For example, about 70 liters of water is utilized during the dark-color reactive dying process of one kilogram of cotton material (Marechal et al., 2012). This wastewater now containing a significant amount of organic dyes is then released into the surface water bodies. (Kalaiarasi et al., 2012) stated in their study in 2012 that about 280,000 tons of textile dyes are discharges into the water resources annually (Kalaiarasi et al., 2012). More so, about 2 to 20 percent of the total dyes wasted (which account for about 10 to

25 percent of the total dye produced) during the textile processes are directly released into the surface water system (Carmen et al., 2012). Polyporus squamosus is a white rot fungus, which causes white rot on wood or trees, and belongs to the basidiomycetes. The mycelia of the organisms can penetrate the cell cavity, and release ligninolytic enzymes to decompose xylon to a white sponge-like mass. The white rot fungus produces three types of extracellular enzymes, and these are nonselective yet effective in attacking lignin. These are often referred to as lignin modifying enzymes (LMEs), and they are lignin peroxidase (LiP), manganese dependent peroxidase (MnP) and laccase (Lac). Although, they effectively break down lignin, these fungi cannot utilize it as an energy source and it is assumed that they degrade it for access to the cellulose in the cell wall. The white rot fungus contains all three enzymes and is therefore able to degrade or mineralize several organic pollutants. The concept for the development of environmental technology using white rot fungus was proposed in 1980s (Bumpus et al., 1995; Aust, 1995).

1.2. The Treatment Methods and Aim of The Study

Biosorption of dyes in textile waste effluents by bacteria or fungi is the best substitute for conventional methods and a very auspicious area of study because of the relatively low cost involved. It has also been shown that microorganisms are able to exploit varieties of organic compounds as precursors for the production of their sources of energy and their own cell materials, even when such compounds are not in high concentrations in the environment (Egli, 1992).

Dyes and the effluent from dye consuming industries results in to the drastic water pollution. Color is the first contaminant to be recognized in the wastewater. The extensive use of the textile dyes has put forth two major problems: one stemming from carcinogenic, mutagenic, allergic and toxic nature of these dyes and other from environmental pollution, like accumulation of dyes, which creates disposal problem; the latter is of much concern (Banat et al., 1997; Bakshi et al., 1999).

This study will therefore add significant contribution to the existing body of knowledge by carrying out a comprehensive approach for identifying the products and intermediaries of textile dye degradation of suitable dye by Polyporus Squamosus and understanding the processes that create such products using a wide spectrum of analytical techniques.

2. LITERATURE REVIEW

Adsorption of Toluidine blue dye from industrial wastewater on the remnants of tea leaf (Firas, 2017). The use of remnants of tea leaf as an inexpensive, profusely and ecofriendly adsorbent has been studied as an alternate substitution of carbon for the removal of dye from industrial effluent. This material was with success accustomed take away the Toluidine blue dye from solution during a batch equilibrium sorption technique. Many investigation have study the economic practicableness of exploitation cheap different materials like rice husk, ash, human hair and tree bark are tested and described to grant heartening leads to many areas of presentation (Weber, 1978), different completely different adsorbents like chitin (Mckay et al., 1980), bittern palm shell (Arami-niya et al., 2010), natural clay (El-Geundi, 1991), Banana shells (Sugumaran et al., 2012), ash (Sumanjit et al., 1998), rice husk (Sumanjit et al., 2001; Malik et al., 2003), walnut shell (Juan et al., 2009), peel (Namasivayam et al., 1996), hazelnut shell (Balsi et al., 1994).

The adsorption of toluidine blue, a basic dye, in to orange peel waste (OPW) was investigated using a batch adsorption technique. A series of assays were undertaken to assess the effect of the system variables (Ridha et al., 2014).

Gypsum was investigated as an inexpensive and efficient adsorbent to remove Toluidine blue from aqueous solution (Rauf et al., 2009).

Clinoptilolite, a natural zeolite, was investigated as an inexpensive and effective adsorbent for the adsorption of Toluidine blue from its aqueous solution (Sibel, et al., 2008).

Polyporus squamosus was tested for it has to absorb Fe (III) ions from solutions. Kinetic and isotherm sorption experiments were conducted to evaluate the effects of contact time, pH, metal concentration, dose of the adsorbent, ionic strength and glucose (Razmovski et al., 2008).

Such wastewater contain both organic and inorganic chemicals consisting of dangerous compounds including dyes and surfactants, and also other contaminants such as dissolved and suspended solid, salts, dispesing agents, acid, alkalis, softeners, fixing agents, and other toxic compounds (Marechal et al., 2012). Organic pollutants released by the Textile industry around the world mostly contaminate surface water. Dyeing and its various finishing stages are the chief polluting processes caused by the textile industry. Some of the pollutants released after the dyeing process are organic molecules with high toxicity and low biodegradability, they contain high biological and chemical oxygen demand, heavy metals, mineral oils, different salts, suspended solids, surfactants, etc. which are released into water bodies in large amounts, thereby polluting the water resources, with long-standing effects on all living organisms and eco-systems at large (Kumar et al., 2012). Though these pollutants may not be toxic sometimes, yet a small coloration of water bodies could make them unappealing and unacceptable to consumers.

Treatment of these water resources has been a major environmental problem. Several technologies have been adopted to remove color and reduce toxicity from these textile effluents, the main technologies presently engaged for color removal are based on the physicochemical processes which include dilution, coagulation and flocculation, adsorption, reverse osmosis treatment, ultra filtration, electrochemical processes, photo-degradation, oxidation, chemical precipitation, and ion-exchange (Banat et al., 1996). Another class of methods depends on the biodegradability of dyes, although dyes are very difficult to biodegrade (Fu et al., 2000).

Although each technique has its advantages, some of them are highly expensive and inefficient in removing the persistent textile effluents from waste resources when used alone. Hence, need to improve efficiency, cost-effectiveness, and eco-friendly treatment systems in recent years (Rasool et al., 2013).

2.1. Waste Water

Water pollution can be defined as any physical, chemical or biological change in water quality which adversely affects living organisms in the environment or which makes a water resource unsuitable for one or more of its beneficial uses (UNEP/WHO, 1988).

According to WHO/UNICEF (2010), globally almost nine hundred million people lack access to safe drinking water. Water quality is affected by changes in nutrients, sedimentation, temperature, pH, heavy metals, non-metallic toxins, persistent organics, pesticides, and biological factors; among many other factors. The discharge of industrial effluent into water bodies is one of the main causes of environmental pollution in many cities, especially in developing countries. Many of these industries lack liquid and solid waste regulations and proper disposal facilities, including for harmful waste (World Health Organization, 2004).

Figure 2.1. Industrial wastewater effluent with neutralized pH from tailing runoff in Peru (Van der Baan et al., 1017).

2.2. Natural Dyes

Natural dyes are organic compounds used to color various products. In before to the year of 1856, normal dyes are extractive from animals, plants, insects and metals sources. Their applications have been limited mainly in food industry, and in view of the increase industrial and population activities, normal dyes do not meet the industrial demand.

2.3. Synthetic Dyes

William Henry Perkin discovered the first synthetic dye in 1856. Dye effluents are results because dyes do not have a full degree of fixation to fiber during dyeing and finishing processes (Pang et al., 2013).

There are different types of dyes used in different industries such as reactive dyes, acid-basic dyes, direct dyes, azo dyes, disperse dyes and vat dyes (Demirbas, 2009). All dyes include the impact of metals such as zinc, copper, chromium, cobalt, and lead in their aqueous solution except disperse dyes. All dyes are water soluble except disperse dyes.

Azo dyes, which represent about one-half of all dyes in common use, are employed as coloring agents in the food, pharmaceutical, and textile industries. The popularity and widespread use of azo dyes is due to several factors. As a group, they are colorfast and encompass the entire visible spectrum, and many are easily synthesized from inexpensive and easily obtained starting materials. In addition, azo dyes are typically amenable to structural modification, and can be made to bind to most synthetic and natural textile fibers.

Dyes are designed to be resistant to light, water and oxidizing agents, so it is difficult to remove them once they are released into the environment. Dye-containing effluents are only slightly decolorized by conventional biological wastewater treatments (Shaul et al., 1991; Wesenberg et al., 2003). Generally, textile dyes in wastewater can be physically or chemically removed by flocculation, adsorption, extraction, filtration or oxidation. Most physical methods simply accumulate and concentrate dyes and create solid waste, but a disposal problem still exists. Chemical oxidation with either peroxide or ozone can destroy dyestuffs effectively but this approach is very expensive.

For bio-treatment applications, it is important to identify the final degradation products as well as intermediates of dyes by fungi because of concern that these compounds may increase the aquatic toxicity of the overall effluent. However, knowledge of fungal degradation mechanisms of organic pollutants including dyes is still lacking. Without insight into the intermediates generated in biodegradation, the true technical potential of white rot fungi cannot be evaluated. The purpose of the study described in this dissertation is to set up analytical methods aiming at identification of products and understanding the processes that create such products. The metabolites of ionic and nonionic azo dyes were identified and quantified. With identification of these products, some fundamental insights into fungal degradation mechanisms and toxicity of wastewater containing azo dyes after decolorization by white rot fungi can be proposed.

Wastewater flowing include synthetic dyes which may cause a latent source of danger to the environment. In view of the health and environmental interests connected with the wastewater flowing, dissimilar separation techniques have been used in the extraction of dyes from aqueous solutions. The separation system can be split into physiochemical, chemical and biological methods. Each separation technique has its have determination in times of resolve, total cost and dye separation activity. A summarization of dye transition separation technique is existing with their disadvantages and advantages in Table 2.1 below.

Table 2.1. The disadvantages and advantages of various dye transition techniques.

Separation Technique	Advantages	Disadvantages
Physiochemical Adsorption	High adsorption capacity for all dyes.	Low surface area for some adsorbents. High cost of adsorbents. Need to dispose of adsorbents.
Ion exchange	No loss of sorbents	Not effective for disperse Dyes.
Membrane Filtration	All dyes with high quality effluent effective.	Fitting for treatment low volume and preparation of clay.
Electro kinetic Coagulation	Feasible economically.	Want enhances treating by filtration, flocculation and production of clay.
Chemical Ozonation	No production of sludge.	High operation cost and half-life is very short (20min).
Fenton reagent	Process and cheap reagent effective.	Elimination problems and clay production.
Photocatalyst	Economically feasible and low operational cost.	Spoil of some article motivation into toxic by-products.
Biological Degradation aerobic	The removal of azo dyes efficient and low operational cost.	Provide suitable environment for growth of microorganisms and very slow process.
Aerobic degradation	By-products can be used as energy sources	Want enhances treating under aerobic case and yield of hydrogen sulfide and methane.

2.4. Response Surface Methodology

Response Surface Methodology (RSM) is a collection of mathematical and statistical techniques useful for analyzing the effects of several independent variables. The main advantage of RSM is the decreased number of experimental trials required to interpret multiple parameters and their interactions. In order to determine a suitable polynomial equation, which would describe the response surface, Response Surface Methodology (RSM) was employed to optimize the process (Myers et al., 2004).

Response surface methodology (RSM) is extensively used optimization methods for reasonable experimental design and process optimization in biosorption research. The optimization of the biosorption process goals at finding the definite conditions such as environmental design parameters for the best possible response, and efficiency removal.

Generally, biosorption is a property of certain types of inactive, dead, microbial biomaterials to bind and concentrate heavy metals from even very dilute aqueous solutions. Biomass exhibits this property, acting just as a chemical substance, as an ion exchanger of biological origin. It is particularly the cell wall structure of certain algae, fungi and bacteria, which was found responsible for this phenomenon. Living as well as dead (metabolically inactive) biological materials have been sought to remove metal ions. It was found that various functional groups present on their cell wall offer certain forces of attractions for the metal ions and provide a high efficiency for their removal (Kuyucak and Volesky, 1988).

2.5. Adsorptions

The operation of adsorption uses the atoms, ions, or molecules of adsorbate to convey and abide to the face of the adsorbent established a thin film. The adsorbate can be in liquid, gas or eliminates solute phases. Adsorption technique can be divided into physical and chemical adsorption. Phys-sorption is an another term of physical adsorption process and it is take control by physical power such as hydrophobicity, Van der Waals forces, polarity, hydrogen bond, dipole-dipole interaction, static interaction.. etc. in the physical adsorption, dirties get stacking on adsorbent surface by the top reminds reacts while chemical adsorption (Langmuir adsorption or Chemisorption) is defined when the adsorbate is chemically determines the adsorbents face due to the change of electrons (Artioli, 2008).

There are various types of physio-chemical separation technique method used in the removal of dyes as part of water and wastewater treatments. Adsorption is deposition of a substance on a surface or intermediate cross-section and is defined as the concentration increases. This process occurs in between any two different phases, such as liquid-liquid, gas-liquid, gas-solid, liquid-solid (Aydin, 2007).

The substance that concentrates at the surface is called adsorbate. While, the material upon whose surface the adsorption takes place is called an adsorbet. The adsorption method generally is used to remove toxic organic pollutants and contaminants from wastewater.

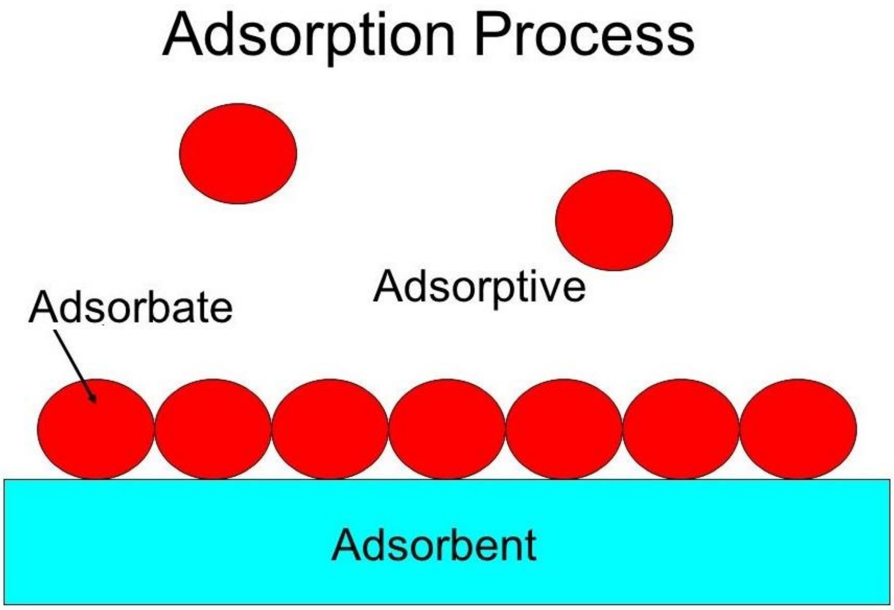

Figure 2.2.Adsorption systems (Butt et al. 2006).

2.5.1. Types of Adsorption

Physical Adsorption

Physical adsorption can be named phys. sorption is due to weak forces such as Vander Waals (weak intermolecular) interactions and electrostatic interactions. For this reason, physical adsorption is also known as Van der Waals adsorption. In this type adsorption, the adsorption substance is not attached to a particular site on the solid surface and it can move over the surface. It may concentrate and form over the layers on the surface of the adsorbent (Muftuoglu, 2003).

Chemical Adsorption

Chemical adsorption can be named chemisorption due to the forces of attraction between the adsorbate and the adsorbent. This adsorption type becomes with a chemical link such as a covalent or ionic bond. Therefore, this type of adsorption is irreversible. To get the matter adsorbed again, the adsorbent environment temperature is highly increased or adsorbent is treated with acidic-basic reactants (Mustafaoglu, 2011).

2.5.2. Adsorption Isotherms

Adsorption happens in a system, which has an affinity between component and solution surface. The component of interest then partitions between the solution and the surface to reach equilibrium. During the process, measuring the decrease of the concentration in solution provides analytical data. Based on this data, if the total amounts of solid and solution in the system are known, the amount of solute adsorbed per unit weight of adsorbing solid can be calculated.(Saint, 1999).

Adsorption process is usually studied through graphs known as adsorption isotherm. Adsorption is the amount of adsorbate on the adsorbent as a function if its pressure or concentration at constant temperature .The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. From the above we can predict that after saturation pressure Ps, adsorption does not occur anymore, that is there are limited numbers of vacancies on the surface of the adsorbent. At high pressure, a stage is reached when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, adsorption is independent of pressure. (Ciuro Juncosa., 2008).

2.5.3. Types of Adsorption Isotherm

Freundlich Isotherm

The Freundlich equation is used to define the distribution of solute between solid and aqueous phases at a point of saturation. The Freundlich equation is an empirical equation employed to describe heterogeneous systems in which it is characterized by the heterogeneity factor 1/n.

Langmuir Isotherm

Langmuir model is an adsorption model for monolayer adsorption, Assumes monolayer coverage of adsorbate over a homogenous adsorbent surface. Irving Langmuir developed and described the monolayer coverage of sorbent surface at a fixed temperature.

2.6. Polyporus Squamosus

Polyporus squamosus is a rather common fungus to find during April and May. Unfortunately, this fungus seems to be more common than morels in some areas, mostly because they are quite a bit larger, up to 2 ft. across sometimes! At least they are much easier to find than morels because they stick out as shelves from the lower portion of dead tree trunks, especially elms. This fungus generally fruits in the spring in most areas, but it is also seen in some places in the fall season. They can grow to be quite large and stick out as shelves from the sides of trees near the base. These shelves have squamules (scales) on the upper surface that give it its species name. The genus name *Polyporus* means "many pores." The pores are lined with basidia that produce basidiospores (Thomas et al., 2001).

Figure 2.3. Polyporus Squamosus (Zmitrvich, 2016).

Polyporus Squamosus, commonly referred to as Dryad's Saddle, grows in overlapping clusters and tiers on broad-leaved trees. (A dryad is a mythical wood nymph.) The fruit bodies appear in summer and autumn. Insects quickly devour these large brackets, and in warm weather, they can decay from full splendor to almost nothing in just a few days.

2.7. Various Physico-Chemical Process Parameters on Adsorption Effect.

2.7.1. Solution pH effect

The set of exchange in pH solution is a main constant factor for solute adsorption because of exchange in face distinguishing of exchange in chemistry and adsorbent of dye.

Such, the adsorption ability of dye depends on the pH of the solution. Generally, the low results of pH solution an increase in the percentage of removal dye anionic because of the electrostatic haul between the positive face charge and anionic dye of the adsorbent (Salleh et al., 2011).

2.7.2. Adsorbent dose effect

The impressive of numerous adsorbent amounts on both cationic and anionic dyes transmission is prove by many researchers to determine the more minimum economical dosage. In general, when the adsorbent dosage increase the dye removal percentage is increasing (Salleh et al., 2011). It was reported that the amount of Indigo carmine dye removal by rice husk was increased with the increase of adsorbent dose (Lakshmi et al., 2009). Also, that the amount of Methylene blue dye removal by pinecone was increased from with the increase of adsorbent mass (Sen et al., 2011).

2.7.3. Temperature effect

In the solution plays, the temperature an important role on the adsorption ability. The adsorption is an endothermic process, if the adsorption capacity increases with increasing temperature. The percentage removal dye of various dyes such as Congo red by organo-attapulgite (Chen et al., 2009), Congo red by modified hectorite (Xia et al., 2011), Congo red by raw pine cone and biomass based activated carbon respectively (Dawood et al., 2014), were increased with the increase of temperature solution. However, the removal dye of Methylene blue by montmorillonite clay (Almeida et al., 2009) and Methylene blue by pinecone (Sen et al., 2011) the adsorption process is an exothermic process because was reported to decreases with the increase of solution temperature therefore the adsorption process is an exothermic process.

2.7.4. Initial dye concentration and amount dosages effect

The initial dye concentration effect plays a main role in the percentage of removal dye and amount of dye-adsorbed and commonly, decrease the percentage of removal dye refers increasing the initial dye concentration, which may be due to the satiate of adsorption place on the adsorbent surface (Dawood et al., 2014). The magnitude of dye adsorption increases with increasing amount dosages at all initial concentrations dye as reported by different researchers (Sen et al., 2011; Purkait et al., 2007; Foo and Hameed, 2011). This is thus because the initial concentration dye supplying the driving force to conquer the durability to the mass convey of dye between the solid phase and aqueous.

2.8. Research objective

The main objective of this research is to investigate the bio-sorption of textile dyes (Toluidine blue) using fungi (*Polyporus Squamosus*) from aqueous medium. In order to achieve the stated aim above, the specific objectives of this research are outlined as follows:

1. Characterization of textile wastewater
2. Evaluation and comparison of several existing textile treatment methods
3. Understanding the processes involve in bio-sorption of Toluidine textile dyes

3. MATERIALS AND METHODS

3.1. Materials

Tolidine blue dye was used. All reagents were of analytical grade of highest purity available and they were used without further purification. Distilled water was also used throughout this study. *Polyporus Squamosus* fungus was collected from Yuzuncu Yil University, Biology Department.

3.2. Instruments

UV-Spectro**:** Thermo, Lambda EZ 150 models/modeled UV Visible adjustable spectrophotometer capable of reading (at 640 nm wavelength).

Precise Balance**:** The PRECISA brand (XB 220A) precision scale, which is protected against air currents by special glass screens, is used. The scale has the ability to measure between 0.0001 – 220g.

pH Meter**:** SCHOTT brand laboratory pH meter capable of precise measurements was used to measure and adjust the pH of the solution to be prepared.

3.3. Biosorbent Preparation And Toluidine Blue Solutions

Natural *Polyporus squamosus* fungus was collected from Yüksekova Territory in Hakkari Region by Yuzuncu Yil University, Biology Department, Van, Turkey. Naturally obtained *Polyporus squamosus* fungi was ground with a mill and sieved to obtain the desired particle size (below 150 µm) and then it was stored in desiccators for further utilization after drying oven at 40°C for 24 h. The specific surface area, pore volume and pore radius were measured by using the Brunauer, Emmett and Teller (BET) method. The BET method has been used for nano, meso, and macro particle sizes for pore size distribution analysis of powder and bulk samples. BET analysis provides precise evaluation of the specific surface area of materials by means of nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyzer. The technique encompasses external area and pore area evaluations to determine the total specific surface area in m2/g, yielding important information for studying the effects of surface porosity and particle size in a variety of applications (Yusuf et al., 2017).

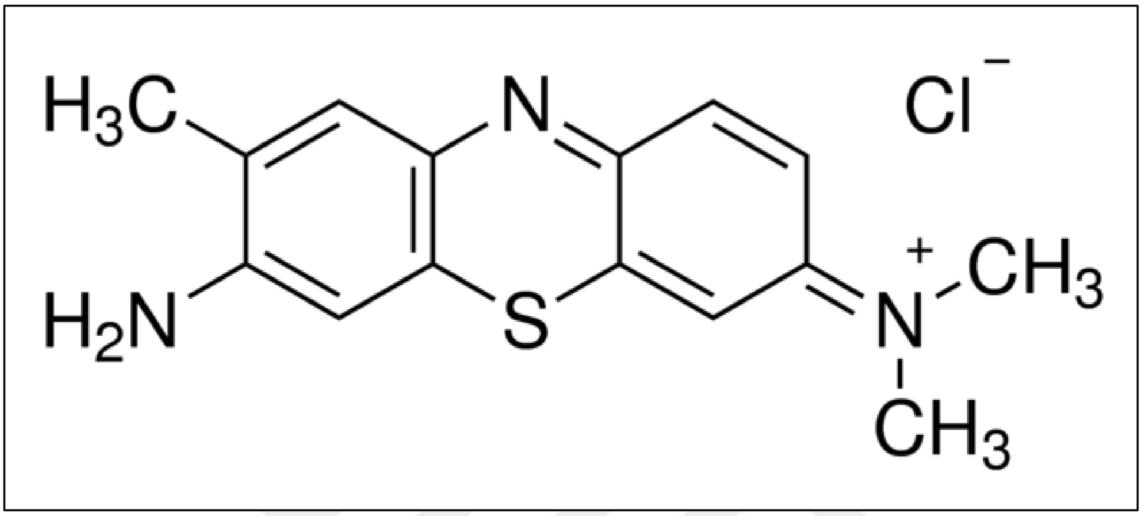

Figure 3.1. Chemical structure of Toluidine blue.

A stock solution of Toluidine blue textile dyes was prepared by dissolving weighed amount of Toluidine blue textile dyes powder in distilled water. The required dilutions were made from stock solution by using different ppm and pH to prepare solutions in the different weight concentrations.

3.4. Batch Biosorption Experiments

All experiments were carried out in batch system using 250 mL flasks containing different mL Toluidine blue textile dyes solution and with temperature-controlled magnetic stirrer. The Toluidine blue textile dyes concentrations remaining in filtration solutions after biosorption was analyzed by using a UV-VIS spectrophotometric. The adsorbed Toluidine blue textile dyes amount was calculated according to the following equation Eq. 1: (Shahan et al., 2010).

$$q_e = \frac{(Co - Ce) * V}{m} \quad \text{..Eq. 1}$$

Where $\mathbf{C_\circ}$ and $\mathbf{C_e}$ are the initial and equilibrium concentrations (mg/L) of Toluidine blue textile dyes solution, **m** is the weight (g) use of the biosorbent and **V** is the volume (L).

3.5. Decision-Making Tree for Landfill Siting

In order to explore the effect of different variables on the response in the region of investigation, a central composite design (CCD) with three variables at three levels was performed. Initial solution pH, temperature (°C), and initial Tb concentration ($C_\circ$) were evaluated as the most effective independent variables and their levels were determined according to the literature (Ṣahan, 2008).

$$\hat{y}_n = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{j=1}^{3} \beta_{ij} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{3} \beta_{ij} x_i x_j \qquad \text{Eq. 2}$$

Where, $\hat{y}$ is the response, $\beta_0$is the constant coefficient, X_i (i = 1–4) are non-coded variables, β_i is the linear, and β_{ii} is the quadratic, and β_{ij} (i and j = 1–4) is the second-order interaction coefficients.

The variance analysis (ANOVA) data were computed by Design-Expert 6.0 (trial version) in order to obtain the interaction between the process variables and the response. The quality of the fit of polynomial model was expressed by the coefficient of determination (R^2), and it is statically significance was checked by the F-test in the same program.

3.6. Adsorption Isotherm Method

3.6.1. Langmuir isotherm

Most common adsorption isotherm equations, including Langmuir, Freundlich, and Dubinin-Radushkevich (D-R), were tested to understand the nature of the adsorption mechanism and the equilibrium conditions (Srividya et al., 2009). The Langmuir isotherm model assumes a monolayer sorption, which takes place at specific homogeneous sites within the biosorbent. The linearized Langmuir isotherm equation is then represented by Eq. 3:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{1}{q_{max}} C_e \quad \text{..........Eq. 3}$$

Where $\mathbf{q_e}$ (mg g^{-1}) and $\mathbf{C_e}$ (mg L^{-1}) are the amount of biosorbed Toluidine blue per unit mass of biosorbend and the Toluidine blue concentration at equilibrium, respectively. In addition, the Langmuir constant, $\mathbf{q_{max}}$ (mmol g^{-1}), is the maximum amount of Toluidine blue per unit mass of biosorbent to form a complete monolayer on the biosorbent surface, while $\mathbf{K_L}$ is a Langmuir constant related to the affinity of the binding sites (L $mmol^{-1}$). Both $\mathbf{q_{max}}$ and $\mathbf{K_L}$ were evaluated from the plot of $\mathbf{C_e/q_e}$ vs. C_e. The essential characteristic of the Langmuir isotherm is a dimensionless constant separation factor $\mathbf{R_L}$, which is a measure of a favorable biosorption process by Eq. 4:

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{..........Eq. 4}$$

Where $\mathbf{C_\circ}$ its highest initial concentration dye (mg/L) and $\mathbf{K_L}$ its Langmuir isotherm constant. The value of separation factor $\mathbf{R_L}$ indicates of the adsorption process as given in Table 3.1.

Table 3.1. The relation between R_L and adsorption

R_L values	Adsorption
$R_L = 1$	Linear
$R_L > 1$	Un favorable
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

3.6.2. Freundlich isotherm

The Freundlich equation is used to define the distribution of solute between solid and aqueous phases at a point of saturation. The Freundlich equation is an empirical equation employed to describe heterogeneous systems in which it is characterized by the heterogeneity factor 1/n.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{.................................Eq. 5}$$

Where, $\mathbf{q_e}$ is an amount of dye adsorbed per unit mass of adsorbent in (mg/g), $\mathbf{K_F}$ is a measure of the adsorption capacity, **1/n** is an indicator of adsorption effectiveness, **Ce** its dye equilibrium concentration (mg/ L).

Table 3.2. Relation between Freundlich coefficient, 1/n value and the type of isotherm adsorption

1/n values	**Adsorption**
$1/n = 1$	Linear
$1/n > 1$	Un favorable
$0 < 1/n < 1$	Favorable
$1/n = 0$	Irreversible

4. RESULTS AND DISCUSSION

4.1. CCD Experiments

Central Composite Design (CCD) assays for optimization of meaningful parameters, such as initial pH, $C_{\circ}$ (mg/L), T (°C), and amount dosages of the biosorbent with the metal solution (experiment time) (min.), were complete to determine the maximum removal of Toluidine blue by resolution particular 7.0 (test conversion). In CCD, amounts of the fully considered parameters are show at three code levels by the platform.

The three coded levels of each parameter were assigned to -1, 0, +1. However the lowest and highest accounts of the parameters were -1 and +1, respectively, the center of the lowest and highest accounts was inspected as the middle mark (0). Both with six responses guide at the middle values to guess the lucid mistake, twenty-four workouts were carried out for optimization.

The statistical meaningful of the square model was foredoomed by the analysis of disparity (ANOVA) as shown in Table 4.2. The account of the degree of limitation (R2 =0.7893) announce that 92% of the variability in the reply is cleared by the specimen. The specimen equation for encoded (real) accounts of the equation sample rigging the empirical outcome is shown in bellow:

Biosorbed amount Toluidine blue dye (mg/g) = +7.47288+ 2.07280 * pH + 4.51980E-003 * Initial conc. ($C_{\circ}$) – 0.65385 * Temperature ($^{\circ}$C) + 251.72573 * Biosorbent dosage (g) – 2.83333E-003 * pH * Initial conc. ($C_{\circ}$) + 0.012750 * pH * Temperature ($^{\circ}$C) + 0.30556 * pH * Biosorbent dosage (g) + 2.09259E-003 * Initial conc. ($C_{\circ}$) * Temperature ($^{\circ}$C) + 3.20370 * Initial conc. ($C_{\circ}$) * Biosorbent dosage (g) + 1.39815 * Temperature ($^{\circ}$C) * Biosorbent dosage (g) – 0.16803 * pH2 – 7.61941E-004 * Initial conc. ($C_{\circ}$)2 + 6.88582E-003 * Temperature ($^{\circ}$C) 2 – 2938.61218 * Biosorbent dosage (g)

Table 4.1. CCD results for Toluidine blue dyes adsorption onto *Polyporus Squamosus* fungi

Run	Initial pH	Initial TB Conc. C_o(mg/L)	Temperature (°C)	Biosorbent Dosage(g)	Biosorbed TB (mg/g)
1	12	50	20	0.1	10.00
2	12	50	50	0.1	21.344
3	7	27.5	35	0.06	9.49
4	7	27.5	35	0.06	8.18
5	7	27.5	20	0.06	7.80
6	2	50	50	0.1	4.00
7	2	50	20	0.01	15.9294
8	12	27.5	35	0.06	12.08
9	12	50	20	0.01	3.35
10	2	5	20	0.1	0.50
11	12	5	20	0.01	1.75
12	2	50	50	0.01	1.70
13	7	50	35	0.06	1.11
14	7	27.5	35	0.01	2.99
15	7	27.5	35	0.06	9.67
16	7	27.5	35	0.06	9.44
17	12	5	50	0.1	2.50
18	7	27.5	35	0.1	12.08
19	2	27.5	35	0.06	15.9294
20	7	27.5	50	0.06	9.85
21	2	5	50	0.01	0.25
22	2	5	50	0.1	17.701
23	7	50	35	0.06	13.89
24	12	50	50	0.01	21.344
25	12	5	50	0.01	2.50
26	12	5	20	0.1	2.25
27	2	50	20	0.1	15.9294
28	7	27.5	35	0.06	9.17
29	2	5	20	0.01	27.7278
30	7	27.5	35	0.06	9.31

A table showing watched expulsion of Toluidine blue against that acquired is shown in Fig. 4.1. The figure explains that the foretell reply from the experiential specimen is in good accord with the spotted datum. Generally, it is necessary to regulate the fitted pattern to insure that it expand a good convergent of the true order.

Except the pattern appears a useful befit, emergence with realization and optimization of the fitted response surface want probable grant bad or misguiding outcome. The remaining play an important function in separate the fill of the sample.

The low p value appears that the second-order quadratic model for watched outcomes is considerable. The amount of the degree of limitation (R^2=0.9073) announces that 86% of the changeable in the react is cleared by the formal (Shahan, et al. 2010).

Table 4.2. Analyses of difference (ANOVA) for Toluidine blue dye removal using Response Surface Quadratic Model.

Origin	Sum of quadrate	Df	Mean quadrate	F Account	p-account Prob > F
type significant	1341.76	14	95.84	8.76	<0.0001
A-Ph	1	5	0.46	0.5087	
B-Initial conc. (C_o)	304.55	1	304.55	27.84	< 0.0001
C-Temperature (°C)	10.89	1	10.89	1.00	0.3343
D-Biosorbent dosage	166.84	1	166.84	15.25	0.0014
AB1.63	1	1.63	0.15	0.7053	
AC14.63	1	14.63	1.34	0.2656	
AD0.076	1	0.076	6.912E-003	0.9348	
BC7.98	1	7.98	0.73	0.4065	
CD14.25	1	14.25	1.30	0.2716	
$A^2$45.15	1	45.15	4.13	0.0603	
$B^2$0.36	1	0.36	0.033	0.8592	
$C^2$6.14	1	6.14	0.56	0.4653	
$D^2$90.61	1	90.61	8.28	0.0115	
Residual	164.11	15	10.94		
Lack of fit significant	144.28	9	16.03	4.85	0.0340
Pure Error	19.83	6	3.30		
Core Total	1505.87	29			

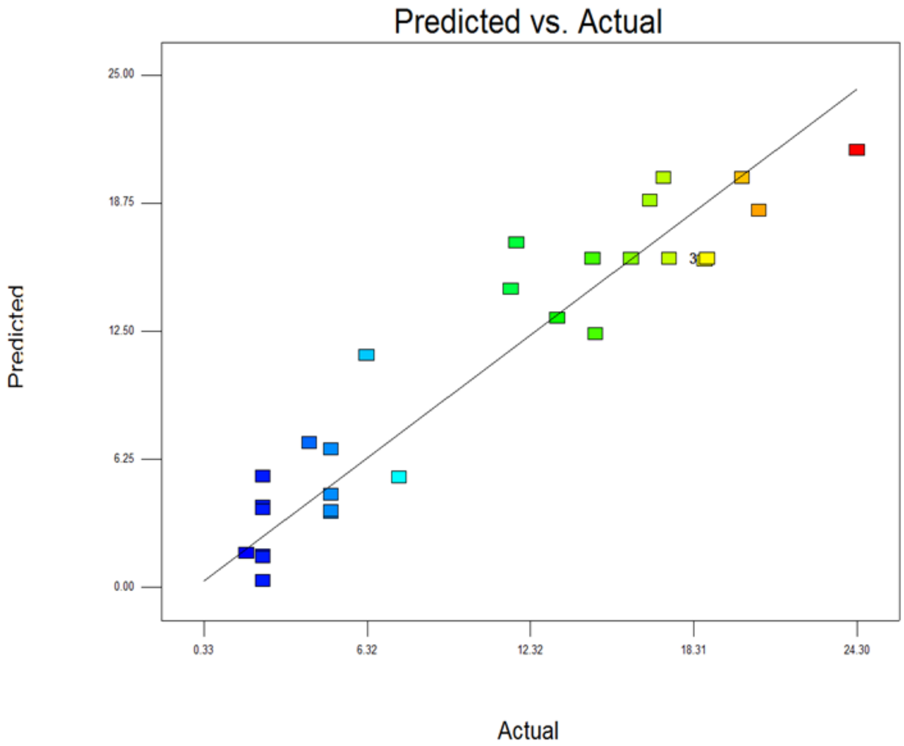

Figure 4.1. The observed TB uptake versus predicted Toluidine blue dye uptake capacity of adsorbent

The figure 4.1 announces that the objected reply from the experiential specimen is in perfect accord with the observed facts. As the dots on the scheme follow an upright line, it can be finished that the precipitate are naturally assorted and facts conversion is not wanted. Whereupon, it insistent that the potential of the empirical facts acquired from increased square specimen for the adsorption of Toluidine blue dyes by *Polyporus Squamosus* fungi is completely favorable.

A scheme offering observed waste of Toluidine blue against that acquired from Eq. 6. is represent in Fig. 4.1. The figure announces that the foreteller response from the experimental sample is in perfect treaty with the observed facts.

Generally it is needful to fruition the fitted sample to guarantee that it supply's a passable sacrificial of the true method. Except the sample widths a passable outfit, emersion with realization and optimization of the suitable response surface will bearable grant weakly or misguiding outcome. Based on this outcome, it can be finished that the experiential datum supply with the foretelled facts studied from Eq. 6. (Myers and montgomery, 2002).

4.2. Adsorbent Amount (Dosage) Effect

In general, the efficacy of different adsorbent doses on both cationic and anionic dyes waste was amount of many investigators to define as nearly economic dosage.

The value of Methylene blue dye waste by pinecone was increased with the increase of adsorbent mass (Sen et al., 2011). So, that the magnitude of Indigo carmine dye waste by rice husk was increased with the increase of adsorbent dose (Lakshmi et al., 2009). The magnitude of Congo red dye waste increased for an increase in adsorbent dose (Kumar et al. 2010).

The adsorbent dosage result of the adsorption of Toluidine blue dyes was deliberate at dissimilar dosages in the solution at pH 12. The adsorption proportion of waste Pb^{2+} and Cu^{2+} ions increased as the dosage of bentonite increased. This may be cleared by the metal ions vying for bordering adsorption places at a lower bentonite dosage. The increase in the adsorption proportion with an increase in adsorbent dosage was due to an increase in lively places on the adsorbent, so easing the breakthrough of metal ions to the sorption places (Abollino et al., 2003).

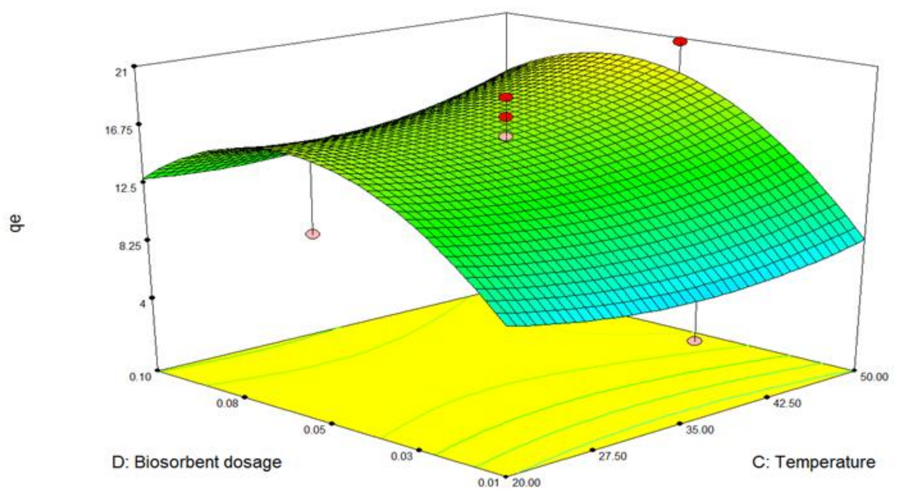

Figure 4.2. Simultaneous effects of adsorbent dosage and temperature on TB waste at constant pH 7 and initial concentration 27.50 mg/L.

Fig. 4.2 offers the synchronous effects of adsorbent dosage and temperature on Toluidine blue dyes waste by *Polyporus Squamosus* fungi. Temperature has a positive effect on Toluidine blue dyes adsorption. Waste of Toluidine blue dyes by *Polyporus Squamosus* fungi gently increased with temperature and gains its ceiling value about 50 ºC. Then waste of Toluidine blue dyes decreased by increasing adsorbent dosage . This is due to the spot that at higher adsorbent dosage, the concentration of the solution drops to a small amount and the method field balance at small amount adsorbed per unit weight of adsorbent.

4.3. Temperature effect

Adsorption operation as a rule is exothermic characteristic so adsorption capability increases with decreasing temperature. The temperature is main for adsorption because it characteristic model of adsorption (Sonmez, A., 2011). The temperature of the solution changes main functional adsorption ability. The adsorption called endothermic process when the adsorption ability increases with increasing temperature. The waste dye of Methylene blue by montmorillonite clay (Almeida et al., 2009) and Methylene blue by pinecone (Sen et al., 2011) was recorded to decreases with the increase of solution temperature where upon the adsorption process is an exothermic process.

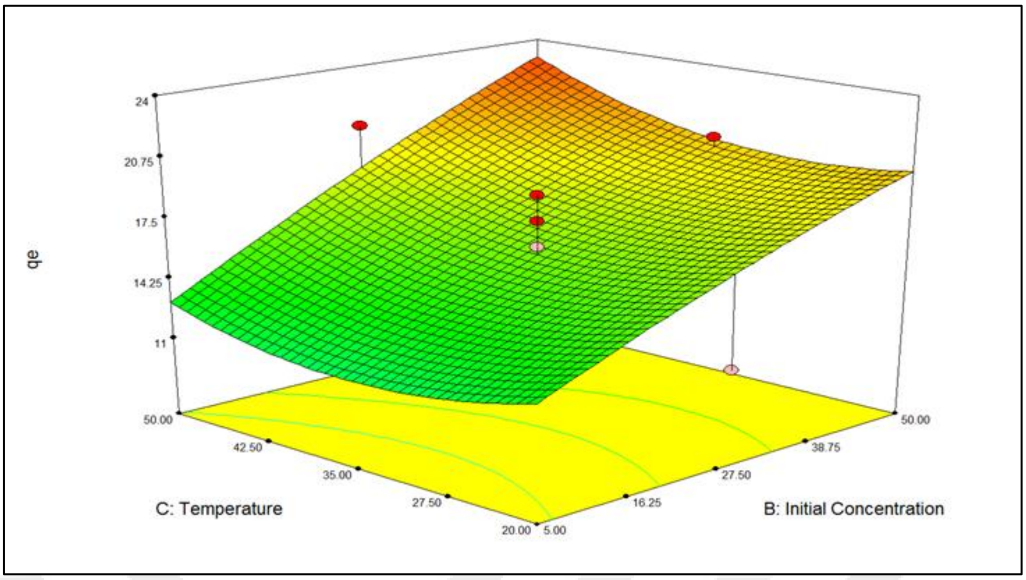

Figure 4.3. Simultaneous effects of medium temperature and initial concentration of TB at constant pH 7 and adsorbent dosage 0.05(g).

Fig. 4.3 represent effects of medium temperature and initial Toluidine blue dyes concentration on dye waste ability of Toluidine blue dyes at constant pH 7 and adsorbent dosage 0.05 g. The waste ability of Toluidine blue dye increased with initial concentration increasing from 5.00 to 50.00 mg/L.

There are reciprocal effects of temperature and initial Toluidine blue dyes concentration on adsorption ability by *Polyporus Squamosus* fungi at a constant pH of 7. As show in Figure 4.3 temperature showed a considerable effect on waste of Toluidine blue dyes onto *Polyporus Squamosus* fungi.

The initial concentration on dye waste supply an main active power to get over all mass convey struggle of Toluidine blue between the solid phase and aqueous medium, wherefore an forward initial concentration of Toluidine blue dye may increase the adsorption ability. It is usually found real to sample the suitable sample to boost that it prepares and acceptable appraisal to the true method.

Toluidine blue dyes waste ability for *Polyporus Squamosus* fungi softly increased with increasing temperature from 20 to 50°C and almost attained to outside account about 35°C. Then adsorption ability of Toluidine blue dyes onto *Polyporus Squamosus* fungi increase with increasing temperature and this resultant appears adsorption is endothermic in circumference. The temperature of solution is the main part of adsorption ability. The adsorption is endothermic process when the adsorption ability increases with increasing temperature were increased with the increase of temperature solution and our mechanisms verified this knowledge as well (Dawood et al., 2014). The increase of technique with the increase in adsorption can be due to a purpose for the Toluidine blue dyes to pertain from the solid phase to the block phase when the temperature of the solutions was increased.

4.4. pH effect

The plurality of substances accomplish with the industry are opposite charged and usually carbons will give greater color elimination with increase in tartness of the solution, the pH of the adsorbent oneself is an main factor, as this may demonstrate the pH of the liquid. The effect of the pH of the solution is a main dominant parameter in the adsorption operation. The pH of a solution from which adsorption happen impacts the range of adsorption. Because, hydrogen and hydroxide ions are adsorbed fully robustly, the adsorption of other ions is impact by the pH of the solution.

Higher pH solution, electrostatic disharmony is found between dye molecules and the negatively charged superficies thus diminish the waste percentage of anionic dyes and adsorption ability (Hameed and Foo, 2011). From advanced research, the eclecticism pH solution of anionic dyes waste such as Congo red by acid modified and raw and interactive blue by chitosan (Sreelatha et al., 2011), Congo red by nut shells charcoal (Kaur et al., 2013), Acid blue 15 by Pomelo skin (Foo and Hameed, 2011), was between (pH 2-4). Then high pH solution consequence in a raise the percentage of cationic waste dye because the positive freight of solution interface will dwindling and the adsorbent surface shows negatively charged (Salleh et al., 2011).

The optimum pH solution on the waste of cationic dyes such as Basic red 46 by pine tree leave (Yagub et al., 2012) and Methylene blue by pine tree leaves was between (pH 9-11) (Deniz and Karaman, 2011).

In the existing action, the adsorption of Toluidine blue dyes on *Polyporus Squamosus* fungi was advised at different pH levels spread from 2.0 to 12.0. At higher pH solution, electrostatic dis harmony is necessitate between the dye molecules and the negatively charged surface, so lessening the percentage waste of anionic dyes and adsorption ability (Hameed and Foo, 2011). The adsorption ability of dye depends on the pH solution. Mostly, low pH solution outcome in augmentation in the anionic percentage dye of waste because of the electrostatic gravitation between the positive surface charge of the adsorption and anionic dye. High pH solution consequence in augmentation in the cationic percentage dye waste because the adsorbent exterior shows negatively charged and positive charge on the solution interface will lower (Salleh et al., 2011).

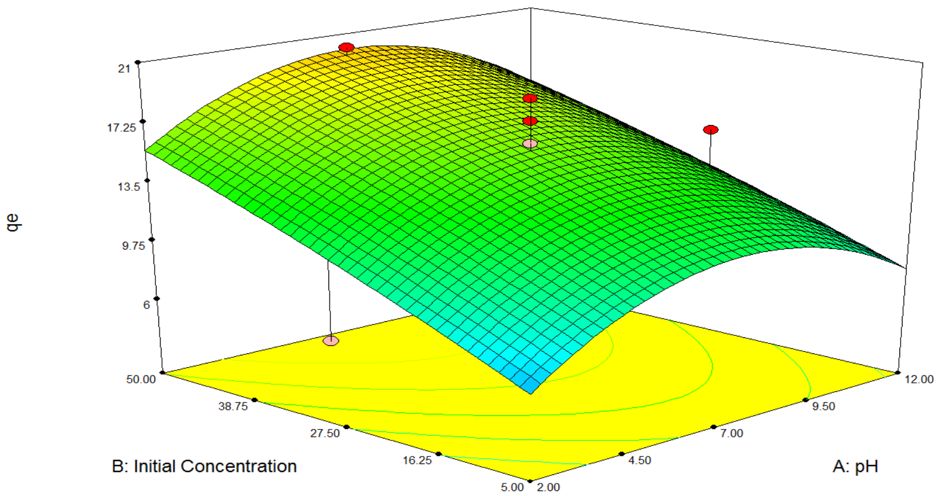

Figure 4.4. Simultaneous effects of and pH and initial concentration (C◦) on TB waste at constant adsorbent dosage 0.05 g and 35°C.

Figure 4.4 offer the adsorption ability of *Polyporus Squamosus* fungi quickly augment with growing C◦ from 5.00 to 50.00 mg/L and nearly connected a maximum at 50.00 mg/L. This outcome can be clarified because of the react of Toluidine blue dye and *Polyporus Squamosus* fungi adsorbent. When C◦ was 27.50 mg/L, the dye understanding change to equilibrium and all positions were satiate with dye. This phase is the systematic adsorption point and the average of addendum of adsorption capacity regularly slows with increasing C◦, at last, the dye uptake ranges balance. At the lower Toluidine blue dye concentration, the proportion of number of moles of dye waste to the present adsorption point is low, and thus the quantity adsorbed per unit adsorbent augment slowly (Bhattacharyya et al. 2008).

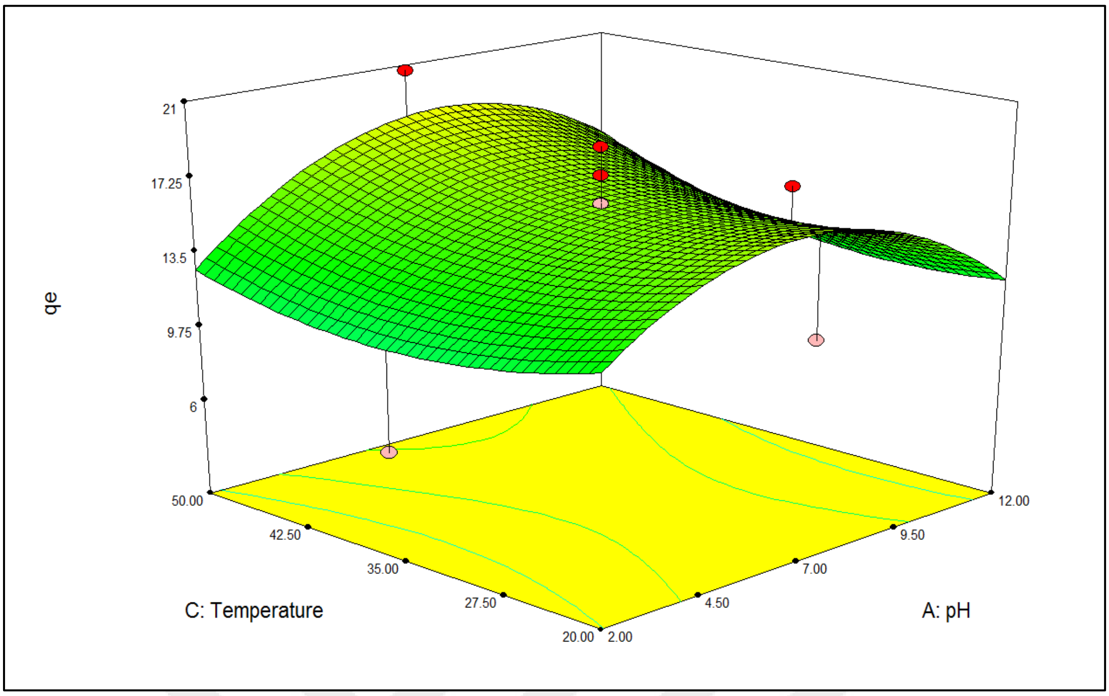

Figure 4.5. Simultaneous effects of temperature and pH on dye waste at constant adsorbent dosage 0.05 g and C◦ of 27.50 mg/L.

The Toluidine blue dye waste ability of biosorbent is unexpectedly excessed when pH of the solution excessed from 2 to 12 as shown in Fig. 4.5. The outcome showed that the utmost waste of dye was done at pH 7. Toluidine blue dyes waste ability for *Polyporus Squamosus* fungi gently excessed with excessing temperature from 20 to 50°C and about arrived to maximum value about 35°C Synchronous impacts of pH and temperature on waste ability of Toluidine blue dye for *Polyporus Squamosus* fungi at a constant initial concentration of 27.50 mg/L are explained in Figure 4.5.

Temperature showed a large impact on waste of Toluidine blue dyes onto *Polyporus Squamosus* fungi. Toluidine blue dyes removal disposition for *Polyporus Squamosus* fungi genially excessed with excessing temperature from 20 to 50°C and about arrived to maximum value about 35°C Synchronous impacts of pH and temperature on waste ability of Toluidine blue dye for *Polyporus Squamosus* fungi at a constant initial concentration of 27.50 mg/L are showed in Figure 4.5.

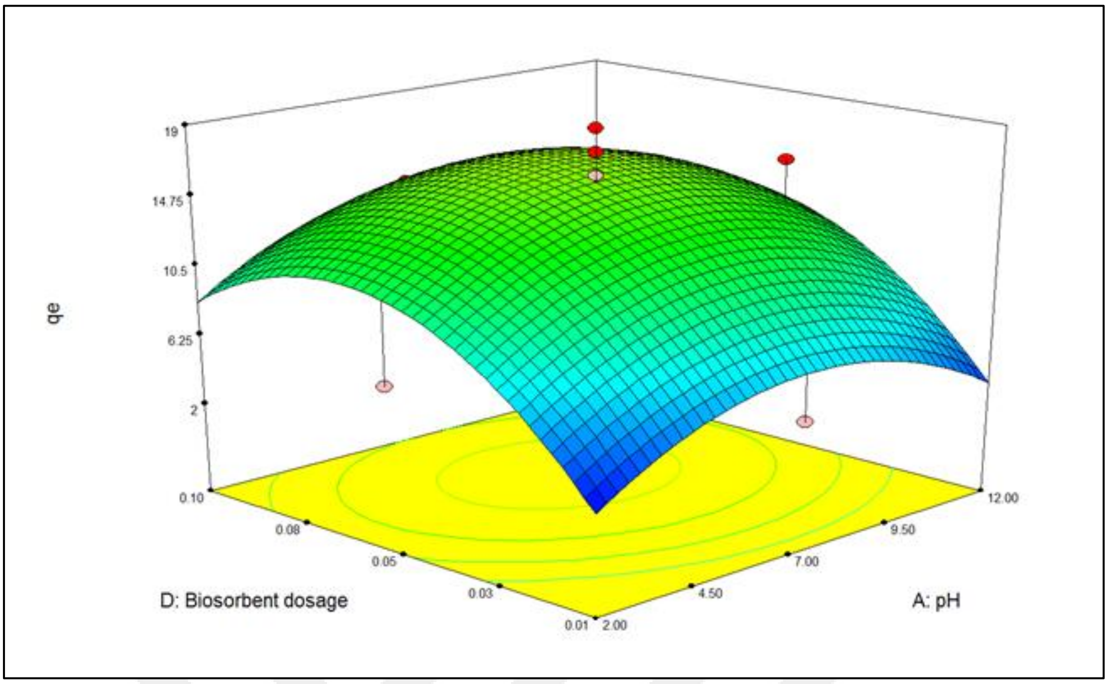

Figure 4.6. Simultaneous effects of adsorbent dosage and pH on TB waste at constant initial concentration of 27.50 mg/L at 35 ºC.

As represented in Fig. 4.6 while waste of Toluidine blue dyes excessed pointedly when pH rose from 2 to 12, waste ability reduce over this pH. Maximum waste was about observed at pH 7. The pH demand of dye understanding is related to both the dye chemistry in solution and the functional groups on the adsorbent surface, which impacts the surface freightage of the adsorbent and the degree of ionization of the adsorbate. Surface charge intensity is regarding to media pH.

At the Point of Zero Charge (PZC), the freightage from cations and anions are similar and total charge of adsorbent is zero (Shahan et al., 2014).

The waste ability of *Polyporus squamosus* fungi quickly excessed when the adsorbent dosage excessed from 0.01 g to 0.1 g and almost attain a maximum at 0.1 g. The excess in waste of Toluidine blue dye with excessing adsorbent dosage can be depicted by the excess in energetic places in the antecedent amount of adsorbent, accordingly fixed that easier penetration of dye waste to active sites. Then waste of Toluidine blue dyes reduced by excessing adsorbent dosage from 0.01 to 0.1 g. For each unit weight of adsorbent this is due to the reality that at higher adsorbent dosage, the initial concentration of the solution breakdown to a lower value and the order connect balance at lower values adsorbed for each unit weight of adsorbent, display that the adsorption sites stay unsaturated (Zhang, et al. 2008).

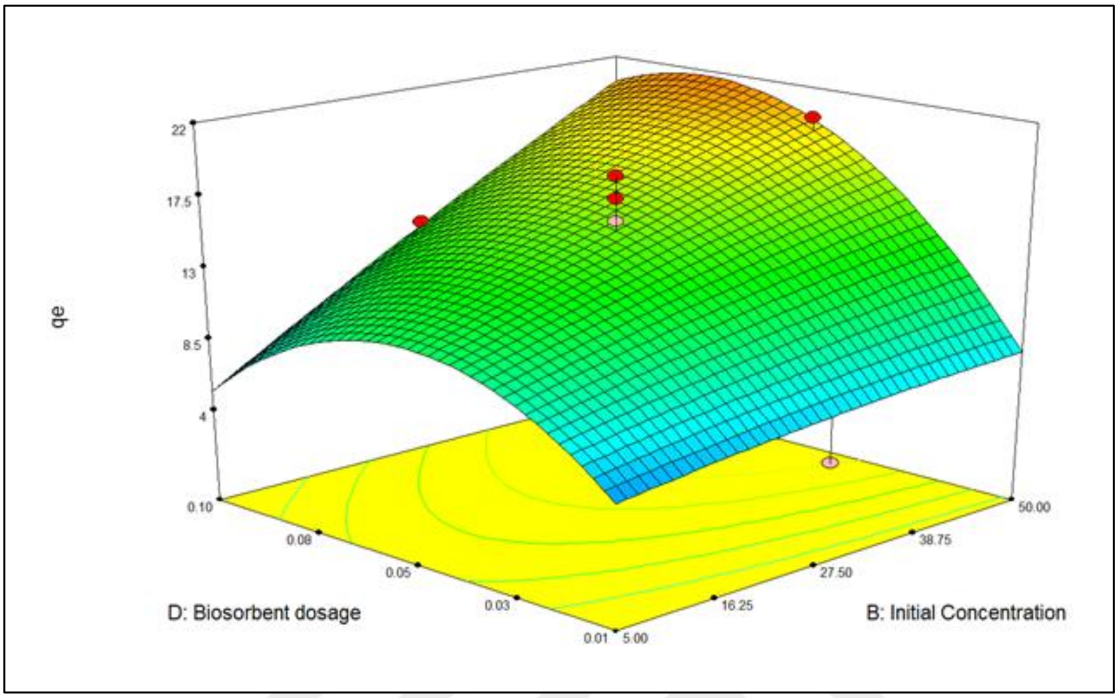

Figure 4.7. Simultaneous effects of adsorbent dosage and initial concentration on TB waste at pH 7 and temperature 35ºC.

Figure 4.7 displays the adsorption ability of *Polyporus squamosus* fungi quickly excessed with excessing C_0 from 5.00 to 50.00 mg/L and about attained a maximum at 27.50 mg/L. This outcome can be clarified because of the interaction of Toluidine blue dye and *Polyporus squamosus* fungi adsorbent. At the lower Toluidine blue dye concentration, the proportion of number of moles of dye waste to the presenting adsorption place is low, and wherefore the amount adsorbed per unit adsorbent excesses tardily.

The waste ability from *Polyporus squamosus* fungi quickly excessed and about attained a maximum at 0.1 g. The excesses in waste of Toluidine blue dye with excessing adsorbent dosage can be clarified by the excesses in strong sites in the forward amount of adsorbent, accordingly fixed that easier penetration of dye waste to active sites (Karimaian et al., 2013).

4.5. Biosorption Isotherm Studies

A linear Langmuir adsorption isotherm is given in fig. 4.8. The values of $\mathbf{q_m}$ and $\mathbf{K_L}$ of linear term of Langmuir adsorption isotherm were studied the slopes and object of the $\mathbf{C_e/q_e}$ with **Ce** according to Eq. 3

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{1}{q_{max}} C_e \quad \text{...Eq. 3}$$

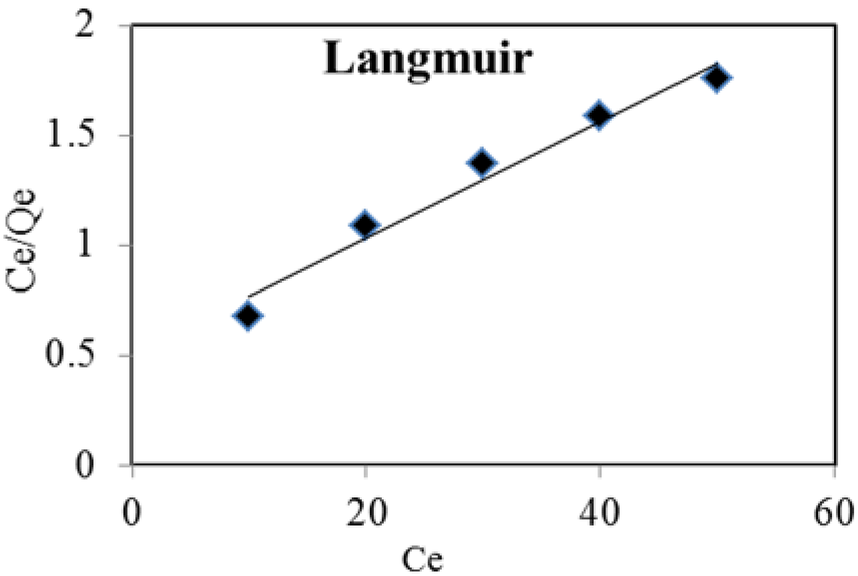

Figure 4.8. Langmuir adsorption isotherm.

The slope and the object agree to 1/n and k_f relatively. It was detected that the plot of ln qe and ln Ce crop a reversible line. In the sitting research the value of connection coefficient (R^2=0.9702) is higher than the Langmuir isotherm value, but the slope is reversible.

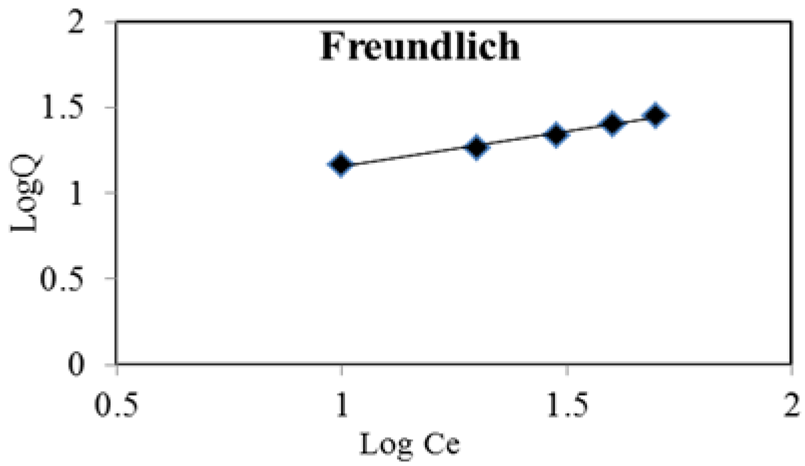

Figure 4.9. Freundlich adsorption isotherm.

Freundlich isotherm model however Langmuir isotherm suppose that enthalpy of adsorption is separate of the amount adsorbed, the experimental Freundlich equation, founded on sorption on heterogeneous surface, can be extract supposition a logarithmic reducing in the enthalpy of adsorption with the excess in the part of taken sites. The Freundlich equation is simply experimental based sorption on heterogeneous surface.

The slope and the object agree to (1/n) and $k_{f,}$ relatively. It was detected that the plot of log q_e and log C_e yields a reversible line (Fig. 4.9). In the sitting research the value of attachment coefficient (R^2 = 0.9878) is higher than the Langmuir isotherm value, but the slope is reversible, that means it isn't Freundlich isotherm model.

Sitting a compare between the Toluidine blue biosorption ability of *Polyporus squamosus* and some biosorbents used in the literature. *Polyporus squamosus* is an cheap biosorbent and is plenty in nature. We can infer that *Polyporus squamosus* has a higher biosorption ability for Toluidine blue than some other natural biosorbents. Due to these properties, *Polyporus squamosus* has large possibility for the waste of Toluidine blue from aqueous media.

Table 4.3. Differentiation between Polyporus Squamosus and other biosorbents used in the literature.

Biosorbent	Toluidine blue Biosorption (mg/g)	References
Aspergillus niger	3.2	(Karunasagar et al., 2003)
Alkaline modified *Penicillium oxalicum var. armeniaca*	270	(Svecova et al., 2006)
Guava bark	3.4	(Lohani et al., 2008)
Streptococcus pyogenes	4.8	(Tüzen et al., 2009)
Garlic (*Allium sativum L.*)	0.65	(Eom et al., 2011)
Ulva lactuca	0.21	(Henriques et al., 2015)
Polyporus squamosus	3.54	(Yusuf et al., 2017)
Polyporus Squamosus	22.8	This study

5. CONCLUSION

The experiential expression used in this research is the traditional quantity process; the *Polyporus Squamosus* fungi collected from Hakkari, Turkey were first used for Toluidine blue waste from an aqueous ambience. The statistical style of RSM, used to optimize the biosorption status, has much usefulness in idiom of estimate and period. It supplies more experiential information and diagrammatical with very small workout needful.

Studies on the waste of organic pollutants by biosorbent such as fungi are exclusive. In increment *Polyporus Squamosus* fungus is an inbred substance that does not make toxic dangerous to have possible for use in unlike place. Biosorption of Toluidine blue from watery surroundings by a new biosorbent, *Polyporus Squamosus*, will fabricate an important contribution to the literature because it is a novel adsorbent-adsorbate gathering.

The Central Composite Design (CCD) in Response Surface Methodology (RSM) was succeeded used to optimize the biosorption adverb for Toluidine blue biosorption onto *Polyporus Squamosus* fungus. A quadratic formal was average in words of initial pH, initial concentration $C_{\circ}$, temperature T ($^{\circ}$C), and time to explain the maximum biosorbed Toluidine blue. With the acquired quadratic formal, the better status for maximum biosorbed Toluidine blue were studied to be 7, 27.5mg/L, 35°C and 0.05g for pH, C, T($^{\circ}$C) and adsorbent dosage, respectively. Beneath the resolved optimal circumstance, the outside amount of biosorbed Toluidine blue and waste yield were studied using the quadratic model to be 22.8 mg/g and 30.22%., respectively. *Polyporus squamosus*, which an active biosorbent for the waste of organic pollutants such as Toluidine blue**.**

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APPENDIX
EXTENDED TURKISH SUMMARY

ESMAIL Liqaa Samir
Yüksek Lisans Tezi, Kimya Mühendisliği Bölümü
Tez Danışmanı: Dr. Öğr. Duygu ALPASLAN
2018, 73 sayfa.

1. ÖZ

Çok miktarda boya ve ağır metal içeren tekstil atıksuları insan sağlığı ve yeryüzü temiz su kaynakları üzerinde bir takım olumsuz etkilere neden olabilirler. Optimizasyon belirli kalite kriterleri, optimum koşullar ve tasarlanan sistemin performansı açısından en iyi çözümü belirlemek için kullanılan bir yöntemdir.

Biyosorpsiyon sürecinin optimizasyonu, mümkün olan en iyi tepki verimi ve boya giderimi için çevresel ve tasarım parametreleri gibi kesin koşulların bulunmasını amaçlamaktadır. Tepki yüzeyi metodolojisi (RSM), biyosorpsiyon araştırmalarında makul deney tasarımı ve proses optimizasyonu için yaygın olarak kullanılan optimizasyon yöntemleridir.

Bu çalışmada, Cevap Yüzey Metodolojisi (RSM) Merkezi Kompozit Dizayn (CCD) başarıyla biyosorbent gibi doğal *Polyporus squamosus* mantarlar üzerine Toluidine tekstil boyalarının adsorpsiyon koşullarını optimize etmek için uygulanmıştır. İlk olarak, *Polyporus squamosus* mantar toz ve kurutma cihazı içerisinde saklanmıştır. Daha sonra Toluidine biyosorpsiyonu etkileyen en önemli parametreler olan pH, Toluidine Konsantrasyonu (Co), Sıcaklık (T) ve biyosorpsiyon duzu (gr) belirlenmistir.

Anahtar kelimeler: Biyosorpsiyon, Toluidin**(**Tekstil Boyaları), Optimizasyon, . *Polyporus squamosus*, Cevap Yüzey Yöntemi.

2. GİRİŞ

Dünya çapında, imal edilmiş 10.000'den fazla kimyasal olarak farklı boyalar vardır. Boya ürünleri dünya üretimi yıllık olarak yaklaşık 7. 108 kg'dır.[Toh, Y.C., Yen, J.J.L., Jeffrey, P.O., Ting, Y.P., 2003]. Bu boya ürünleri çoğunlukla tekstil sanayisi tarafından kullanılmaktadır .Boya ve boya ürünleri ayrıca kağıt endüstrileri, tabakhaneler, ilaç sanayisi, gıda ambalaj sanayisi ve galvanik gibi sektörlerde kulanılmaktadır. İmalat boya ve uygulama boya ağırlıklı olan bu sektörlerde atıklar sıvı, gaz veya katı atıklar olabilir. [Parvathi, C. Maruthavanan, T. and Prakash, C. 2009].Çok miktarda Su, tekstidel boyama işlemi ve yıkama sırasında kullanılır.Örneğin; yaklaşık bir kilogram pamuk malzemesi için 70 litre su kullanılır.[Marechal, A.M.L., Križanec, B., Vajnhandl, S., Valh, J.V., 2012].

Organik boyaları önemli miktarda içerdiği atık su daha sonra yüzey kütlelerinin içine salınır. [Kalaiarasi, K., Lavanya, A., Amsamani, S., Bagyalakshmi, G., 2012] Tekstil boyaları yıllık yaklaşık 280.000 ton su deşarjlar.2012 yılında yapılan çalışmada belirtilmiştir. Boyaların yaklaşık yüzde 2 ile yüzde 20'si tekstil boyası sırasındaki süreçlerde doğrudan su yüzeyine salınır.[Carmen, Z., Daniela, S., 2012]. Bu atık su boyalar ve yüzey aktif içeren tehlikeli bileşikler aşağıda oluşan organik ve inorganik kimyasal maddeleri içerir, çözülmüş ve süspanse edilmiş katı maddelerin, tuzların, asitlerin, yumuşatıcıların, sabitleme ve diğer toksik bileşikler gibi kirletici madeler içerir.[Marechal, A.M.L., Križanec, B., Vajnhandl, S., Valh, J.V., 2012].

Boya atıkları yeterli tedavi uygulandığında yada çok uzun süre çevrede kaldıktan sonra kompozisyon değişiklikleri ile onkojenik ve mutajenik olabilir[Kalaiarasi, K., Lavanya, A., Amsamani, S., Bagyalakshmi, G., 2012]. Bu boyalardan başka kullanılan boyaların yüzde 60'tan fazlası azo boyalar olduğu saptanmıştır, Bu azo boyalarının anaerobik durumda kanserojen diazonyum tuzları halinde azaltılabilir. [ETAD, 2003].Boya atıklarındaki su kütleleri boşaltılır, bu nedenle, kirlilik oluşur. Alıcı su kaynaklarının içine işlenmemiş tekstil atıklarının doğrudan su kütleleri halinde olması güneş ışığı girmesini azaltır, arınma için gerekli akuatik hayat esansiyel büyümesinin engellenmesi, çözünmüş oksijen seviyesinin düşmesine neden olan, ve fotosentetik etkinlikte bir azalmaya yol açan, akut toksik reaksiyonlar yoluyla su kalitesini düşürür ve hem çevre hem de flora ve fauna büyümesinde rahatsızlığa neden olur

Bu araştırmanın temel amacı, sulu ortamdan *Polyporus squamosus* kullanarak tekstil boyalarının biyosorpsiyonunu (Toluidine) araştırmaktır. aşağıdaki gibi yukarıda belirtilen amaca ulaşmak için, bu araştırmanın özel hedefleri özetlenmiştir :

1. tekstil atıksu karakterizasyonu .
2. Değerlendirme ve birkaç mevcut tekstil tedavi yöntemlerinin karşılaştırılması .
3. *Polyporus squamosus* kullanarak Toluidine tekstil boyalarının süreçleri anlama ve biyosorpsiyona katkisi

3. MATERYAL VE YÖNTEM

Biyosorbent hazırlama ve Toluidin tekstil boyaları çözümleri

Doğal *Polyporus squamosus* mantar Yüzüncü Yıl Üniversitesi, Biyoloji Bölümüni, Van, Türkiye tarafından Hakkari Bölgesinde Yüksekova Bölgesi toplanmıştır. Doğal olarak elde *Polyporus squamosus* mantar, bir değirmen ile öğütülmüştür, ve istenen parçacık boyutunu elde etmek üzere elekten (150 µm altında), ve daha sonra 24 saat için 40 ° C'da fırın kurutulduktan sonra daha sonra kullanılmak üzere desiccators depolandı. spesifik yüzey alanının, gözenek hacmi, gözenek çapı Brunauer kullanılarak ölçülmüştür,

Toluidin tekstil boyalarının bir stok çözeltisi, damıtılmış su toluidin Tekstil boya tozunun tartılmış bir miktarının çözülmesiyle hazırlanır. Gerekli dilüsyonları farklı ağırlık konsantrasyonlarda çözümler hazırlamak için farklı ppm ve pH değeri kullanarak stok çözeltisinden yapılmıştır.

Biyosorpsiyon Deneyleri

Tüm deneyler, farklı ml Toluidine tekstil boya çözeltisi ve sıcaklık kontrollü bir manyetik karıştırıcı ile ihtiva eden 250 mL'lik şişeler kullanılarak toplu bir sistemde gerçekleştirilmiştir .Biyosorpsiyonu sonra filtrasyon Çözeltilerin kalan Toluidin tekstil boya konsantrasyonları, bir UV-VIS spektrofotometrik kullanılarak analiz edilmiştir. Adsorbe Toluidin tekstil boyalarının miktarı aşağıdaki denkleme göre hesaplanmıştır [T. Şahan et al. 2014, 2010].

$$q_e = \frac{(C_0 - C_e) * V}{W} \quad (1)$$

C_0 ve C_e başlangıçtaki ve denge konsantrasyonları Toluidin tekstil boyaları çözeltisi (mg / L) olduğu, sırasıyla, V ortamı (L) ve W, hacmi, 5 g / L'de sabit kullanılan biyosorbentni, ağırlığı (g) olduğu , Reaksiyon karışımı içinde kullanılan.

Deney tasarımı ve optimizasyonu

RSM CCD de ikinci dereceden modeli takılması için en popüler seçimdir. Dört değişken için deneylerin sayısı vardı 30 (= 2k + 2K + 6), Burada k bağımsız değişkenlerin sayısı. Yirmi dört deney saf hatayı değerlendirmek için merkez değerlerinde altı tekrarlamalı (sıfır seviyesi) ile güçlendirildi.

4. SONUÇ VE TARTIŞMA

Sonuç olarak, bu çalışmada Polyporus squamosus biyosorbentin katyonik boyalara karşı seçici davranış gösterdiği gözlenmiştir. Deney şartları altında Polyporus squamosus TB maksimum absorplama kapasitesinin, 22.8 mg/g olarak hesaplanmıştır. Bununla birlikte kompozit hidrojelin boya absorpsiyonunun Langmiur izotermine tam olarak uyduğu tespit edilmiştir.

CURRICULUM VITAE

Liqaa Samir ESMAIL, was from Duhok province of Iraq. She was born on Mosul in 1977. She completed elementary, and High Schools in Mosul, after that she received a bachelor's degree in Science / Chemistry Department, University of Mosul, 2000, and she received a Higher Diploma in General Chemistry, 2008. She got admission in Van Yuzuncu Yil University in Turkey at February of 2016 and began graduate studies at Institute of Applied Science in Faculty of Engineering in the Department of Chemical Engineering during the years (2015-2018).

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ACCEPTANCE and APPROVAL PAGE

This thesis entitled "OPTIMIZATION OF TOLUIDINE BLUE BIOSORPTION CONDITIONS FROM AQUEOUS SOLUTIONS BY [*Polyporus squamosus*] FUNGI AS ABSORBENT WITH RESPONSE SURFACE METHODOLOGY" presented by Likaa Samir İSMAİL under supervision of Asst. Prof. Duygu ALPASLAN in the