Biosorption of Priority Pollutants of Petroleum Refinery Wastewater

Deen Adnan Sheikha

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"BIOSORPTION OF PRIORITY POLLUTANTS OF PETROLEUM REFINERY WASTEWATER"

By
Deen Adnan Sheikha

A Thesis submitted to
United Arab Emirates University
In partial fulfillment of the requirements for the Degree of M.Sc. in Water Resources

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ARE: Average Relative Error.
b: Coefficient related to the affinity between the sorbent and sorbate (l/mg).
B_D: Dubinin-Radushkevich isotherm constant, l/J².mol².
BOD: Biological Oxygen Demand, mg/l.
C_e: Equilibrium concentration of sorbate (mg/l).
C_i: Initial concentration of sorbate (mg/l).
COD: Chemical Oxygen Demand, mg/l.
E: Mean free energy of sorption, kJ/mol.
EPA: Environmental Protection Agency.
ERRSQ: Sum of the Squares of the Errors.
HPLC: High Performance Liquid Chromatograph.
HYBRD: Composite Fractional Error Function.
K: Freundlich isotherm constant.
MPSD: Derivative of Marquardt's Percent Standard Deviation.
PAH: Poly Aromatic Hydrocarbons.
ppm: Part per million.
Q: Sorbate uptake (mg/g).
Q_cal: Calculated sorbate uptake (mg/l).
Q_D: Dubinin-Radushkevich isotherm constant, mmol/g.
Q_e: Experimental sorbate uptake (mg/l).
Q_max: Maximum sorbate uptake under given conditions (mg/g).
R: Universal Gas Constant, 8.314 J/mol °K.
R²: Statistical linear coefficient of determination (the square of the correlation, R).
R_L: Dimensionless Separation Factor.
T: Absolute Temperature, °K.
V: Volume of sorbate (L).
To My Faithful Husband Ali

And

My charming Daughter Mariam
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ABSTRACT

Heavy metals and organic materials pollution in the aquatic system have become a serious threat today. Zinc, phenol and naphthalene are common environmental contaminants. The fate and transport of these chemicals must be sufficiently understood to predict detrimental environmental impacts and to develop technically and economically appropriate remedial action to minimize environmental degradation. In this study, microbial biomass has emerged as an option for developing economic wastewater treatment. Dead algal biomass may passively sequester metals and organic materials by the process of biosorption from dilute solutions, where biomass functions as an ion exchanger by virtue of various reactive groups available on the cell surface such as, carboxyl. This biosorption technology has advantages of low operating cost.

The potential use of blank alginate beads, and immobilized dead algal cells for the removal of zinc, phenol and naphthalene from aqueous solutions was investigated. It was found that the biosorption capacities were significantly affected by solution pH. Dynamic and isotherm experiments were carried out at the optimal pH 5.0, 11.0 and 4.0 for zinc, phenol and naphthalene, respectively. The zinc removal rate was rapid and the maximum zinc uptake occurred within the first 30 min in both cases of blank alginate and immobilized algal cells. On the other hand, the equilibrium uptake was attained within the first 5 min in the case of phenol and naphthalene. The equilibrium data for the biosorption of zinc ions, phenol and naphthalene onto both sorbents could be adequately fitted by to the Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm equations. It was also found that the presence of other pollutants, such as citric acid, decreased the uptake of zinc, phenol, or naphthalene, and this increase was function of the other pollutant concentration. The sorption of zinc ions, phenol or naphthalene from refinery simulated wastewater was found to follow pseudo-second order kinetics.
Chapter 1

Introduction

The overall performance of the UAE’s economy is heavily dependent on oil exports, which account for nearly 30% of total gross domestic product (GDP). Growth in real GDP was 4.0% in 2003, partially due to higher crude oil prices, and it is projected to reach 4.2% in 2004. The non-oil segment of the UAE’s economy and exports is experiencing strong growth, particularly the petrochemicals and financial services sectors. The UAE contains proven crude oil reserves of 97.8 billion barrels, or slightly less than 10% of the world total. Abu Dhabi holds 94% of this amount, or about 92.2 billion barrels. Dubai contains an estimated 4.0 billion barrels, followed by Sharjah and Ras al-Khaimah, with 1.5 billion and 100 million barrels of oil, respectively. The UAE’s current OPEC production quota is 2.14 million bbl/d, and its crude oil production in January 2004 was 2.25 million bbl/d. The UAE’s total production capacity is 2.50 million bbl/d, making it second only to Saudi Arabia for excess production capacity among OPEC member states (EIA, Country Analysis Brief, 2004).

Oil refineries like most industries use enormous quantities of water. The excess amounts of water contaminated with hazardous chemicals might be recycled, reused, treated, transported or released. Environmental regulatory agencies are beginning to embrace comprehensive solutions to facility permitting and enforcement issues. Petroleum pollutants of wastewater require careful treatment before being discharged into the receiving bodies of water. These wastes may have extreme impact on the quality of land, air, and water (Sawalha, 2003).

Demirci et al. (1998) reported the characterization of Kirikkale refinery wastewater in Turkey. Table 1.1 shows the gross parameters and only specific parameters for phenol was presented. In addition to this study, other studies covered in literatures revealed that large number of organic chemicals and heavy metals are found in the refinery wastewater. These chemicals have been
considered as priority pollutants based on their acute and chronic toxicity levels. Huge quantities of refineries wastewater are discharged annually into the Arabian Gulf not only from UAE facilities but also from other oil-producing countries in the region (Sawalha, 2003). Therefore, there is a need to identify wastes released from refineries and develop treatment technologies based on local materials suitable for the harsh environment of the UAE.

Table 1.1 Chemical characteristics of wastewater of Kirikkale refinery (Demici et al., 1998).

<table>
<thead>
<tr>
<th>Parameter</th>
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<tr>
<td>COD (mg O₂/l)</td>
<td>800</td>
</tr>
<tr>
<td>BOD</td>
<td>350</td>
</tr>
<tr>
<td>COD / BOD ratio</td>
<td>2.3</td>
</tr>
<tr>
<td>Oil (mg/l)</td>
<td>3000</td>
</tr>
<tr>
<td>Phenols (mg/l)</td>
<td>8</td>
</tr>
<tr>
<td>Sulfites (mg/l)</td>
<td>17</td>
</tr>
<tr>
<td>Suspended solids (mg/l)</td>
<td>100</td>
</tr>
<tr>
<td>pH</td>
<td>6.5-8.5</td>
</tr>
</tbody>
</table>

Many processes have been used for the removal of heavy metals. These include chemical precipitation, coagulation, and solvent extraction, membrane separation, ion exchange; reverse osmosis and adsorption can be applied. For dilute concentration of heavy metals, only ion exchange, reverse osmosis, or adsorption can be used. However, ion exchange and reverse osmosis have high operating cost, which makes adsorption a better alternative for heavy metals removal. For refinery wastewater that contains organic and inorganic species; many treatment processes are applied, for instance anaerobic/ aerobic, flocculation/flotation, flocculation/coagulation polished by adsorption, and oxidations (Demireci et al., 1998, Sokol, 2003, Jou and Huang, 2003, Wilberg et al., 2000). The biosorption
technique, which involves using sorbents of biological origin (Volesky, 2003), offers a promising polishing technique in the treatment of refinery wastewater.

1.1 Objectives

The objective of this work is to investigate the technical feasibility of using immobilized inactive algal biomass for the removal of zinc ions, phenol, and naphthalene from aqueous solutions. The effects of different parameters, such as initial pH, shaking time, and initial zinc ions, phenol, or naphthalene concentrations on the sorption capacity will be investigated. Comparison between sorption on blank alginate and immobilized dead algal biomass will also be investigated. Adsorption kinetics and adsorption equilibrium isotherms will be analyzed using different isotherm models. The effects of the presence of other pollutants on the sorption of zinc, phenol, and naphthalene will also be investigated.

1.2 Thesis Structure

This M. Sc. thesis has seven chapters. The first chapter is an introductory description of the petroleum refining wastewater, and the main objectives are described. In Chapter 2, a literature review on zinc, phenol, and naphthalene treatment methods is presented. Chapter 3 covers the isothermal modeling including Freundlich, Langmuir, and Dubinin-Radushkevich. Materials used in this project and the experimental procedure and analysis are presented in Chapter 4. In Chapter 5 the results of removal of zinc using immobilized dead algal cell are presented, while biosorption of phenol and naphthalene on immobilized algal cells are discussed in Chapter 6. Finally, the main conclusions and recommendations are presented in Chapter 7.
Chapter 2

Literature Review

2.1 Introduction

A supply of clean water is an essential requirement for the establishment and maintenance of diverse human activities. Water resources provide valuable food through aquatic life and irrigation of agricultural production. However, liquid and solid wastes produced by human settlements and industrial activities pollute most of the water resources throughout the world. As pointed out by the United Nation (UN) report (2000) (Pena-Varon, 2002), the life sustaining means offered by nature for our survival are being seriously degraded and disrupted by our own everyday activities. Fertilizer run-off and chemical pollution threaten both water quality and public health. More than 20 percent of freshwater fish stocks are vulnerable or endangered due to pollution or habitat modification. About half of the world's population lacks adequate sanitation and this has resulted in rivers downstream from large cities in developing countries being barely cleaner than open sewers. This situation causes an estimated 80 percent of all diseases in the developing world with an annual death quota of 5 million lives. Hence, the provision of safe water and adequate sanitation to all will greatly contribute to the reduction of disease burden and life saving in developing countries (Pena-Varon, 2002).

Domestic and industrial wastewaters contain a large number of potentially harmful microorganisms and chemical compounds. The discharge of raw wastewater into the aquatic environment may cause serious damage to many forms of life as a result of oxygen depletion in the receiving water bodies. Additionally, the discharge of raw domestic wastewater poses a potential risk for the transmission of a large number of water-related diseases. This situation has produced a growing worldwide awareness of the need for more effective sewage treatment methods. Refineries and surface petroleum operations are potential
major contributors to ground water and surface water contamination. Some refineries use deep-injection wells to dispose of wastewater generated inside the plants, and some of these wastes end up in aquifers and groundwater. Wastewater in refineries may be highly contaminated given the number of sources it can come into contact with during the refinery process (such as equipment leaks and spills and the desalting of crude oil). This contaminated water may be process wastewaters from desalting, water from cooling towers, stormwater, distillation, or cracking. It may contain oil residuals and many other hazardous wastes. This water is recycled through many stages during the refining process and goes through several treatment processes, including a wastewater treatment plant, before being released into surface waters. The wastes discharged into surface waters are subject to state discharge regulations. These discharge guidelines limit the amounts of phenol, heavy metals, sulfides, ammonia, suspended solids and other compounds that may be present in the wastewater. Although these guidelines are in place, sometimes significant contamination from past discharges may remain in surface water bodies (Hazardous Substance Research Centers, 2003).

In 1978, the United States environmental protection agency (USEPA) prepared a list of 129 organic and inorganic pollutants found in wastewater that constitute serious health hazards. This list, known as the Priority Pollutants List, includes the following thirteen metals: antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc. Unlike organic compounds, metals are non-biodegradable and, therefore, must be removed from wastewat ter. Zinc is present in the air, soil, water, and in almost all the food. Zinc is naturally released into the environment, although industrial activities are mostly responsible for zinc pollution. Elevated levels of zinc may come from a variety of sources like mining and foundry activities, zinc, lead, and cadmium refining, steel production, carbon combustion, and solid waste incineration. Zinc is commonly used to coat iron and other metals for the prevention of oxidation. Various zinc salts are industrially used in wood preservatives, catalysts, photographic paper, accelerators for rubber vulcanization, ceramics, textiles, fertilizers, pigments, and batteries. Water reservoirs are contaminated by the run-off from these industries. Other sources of metallic zinc
traces in drinking water are water treatment processes and pick-up of metallic ions during storage/distribution. These toxic metals cause accumulative poisoning, cancer, brain damage, etc., when they are found above the tolerance levels. According to few surveys from the public health services of different countries, significant number of people has been exposed to the hazards of excess metals in the municipal water supplies (Agrawal and Pandey, 2004).

Traditional treatment methods for removing zinc from wastewater include chemical solvent extraction (Kongolo et al., 2003; Preston and du Preez, 2000), chemical precipitation (Veeken et al., 2003), membrane filtration (Srisuwan and Thongchai, 2002), ion exchange (Kurama and Catalşarik, 2000), and adsorption (Ramos et al., 2002; Mohan and Singh, 2002; Peric et al., 2000; Galiatsatou et al., 2002; Aslam et al., 2004). For dilute metal concentration, ion exchange, reverse osmosis and adsorption can be applied. However ion exchange and reverse osmosis have high operating cost, which makes adsorption a better alternative for heavy metals removal (Abu Al-Rub et al., 2004).

Phenol and substituted phenols are toxic organic pollutants commonly present in industrial waste streams especially in industrial wastewater from oil refineries, coal conversion plants, petrochemicals, polymeric resins, coal tar distillation, pharmaceuticals (Khalid et al., 2004). Typical concentrations of phenols present in waste water of various industries are: refineries (6–500 mg/l), pulp and paper industries (0.1–1600 mg/l) (Li et al., 2004). Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health. Stringent US Environmental Protection Agency (EPA) regulations call for lowering phenol content in the wastewater to less than 1 mg/l (Banat et al., 2000). Humic consumption of phenol contaminated water can cause severe pain leading to damage of the capillaries ultimately causing death (Rao and Viraraghavan, 2002).

Traditionally, biological degradation (Gonzalez et al., 2001; Rao and Viraraghavan, 2002; Alsawalha, 2003; Monteiro et al., 2000; Bandhyopadhyay et al., 2001; Godjevargova et al., 2003), adsorption (Khalid et al., 2004; Banat et al.,
2000; Aksu and Yener, 2001), solvent extraction (Li et al., 2004; Olejniczak et al., 2005), and precipitation (Shen, 2002; Ozbelge et al., 2002), are the most widely used methods for removing phenols from wastewater.

Naphthalene is a poly aromatic hydrocarbons (PAHs) that has many industrial uses and is a major component of the coal and tar-based industries. It has been detected in soil, oil contaminated sediments, and both industrial and urban wastewater. Naphthalene has also occasionally been isolated as contaminant at waste sites and was classified as a priority pollutant by the U.S. Environmental Protection Agency (1992) (Nigam et al., 1998). To protect aquatic life, the permissible concentrations of naphthalene are 2.3 and 0.6 mg/l on acute and chronic toxicity, respectively. Naphthalene is moderately toxic by subcutaneous route, and poisoning of naphthalene may occur by ingestion of large doses, inhalation, or skin absorption (Vipulanandan and Ren, 2000). Biological degradation (Kozlova et al., 2004; Nigam et al., 1998), adsorption (Lee and Kim, 2002; Chang et al., 2004), chemical oxidation (Shiyun et al., 2003), are the most widely used methods for removing naphthalene from wastewater.

2.2 Adsorption

The use of solids for removing substances from either gaseous or liquid solutions has been widely used. This process, known as adsorption, involves nothing more than the preferential partitioning of substances from the gaseous or liquid phase onto the surface of a solid substrate. Adsorption phenomena are operative in most natural physical, biological, and chemical systems, and adsorption operations employing solids such as activated carbon and synthetic resins are used widely in industrial applications and for purification of waters and wastewaters.

The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate. Adsorption is thus different from absorption, a process in which material transferred from one phase to another (e.g.
liquid) interpenetrates the second phase to form a "solution". The term sorption is a general expression encompassing both processes.

Activated carbon is the most widely and effectively used adsorbent. A typical activated carbon particle, whether in a powdered or granular form, has a porous structure consisting of a network of interconnected macropores, mesopores, and micropores that provide a good capacity for the adsorption of organic molecules due to its high surface area. The surface chemistry of activated carbon and the chemical characteristics of adsorbate, such as polarity, ionic nature, functional groups and solubility determine the nature of bonding mechanisms as well as the extent and strength of adsorption. A variety of physicochemical mechanisms/forces, such as Van der Waals, H-binding, dipole-dipole interactions, ion exchange, covalent bonding, cation bridging and water bridging, can be responsible for adsorption of organic compounds in activated carbon (Aksu and Yener, 2001).

In spite of these characteristics, activated carbon suffers from a number of disadvantages (Aksu and Yener, 2001):

- It is quite expensive and the higher the quality, the greater the cost.
- Both chemical and thermal regeneration of spent carbon is expensive.
- Impractical on a large scale and produces additional effluent and results in considerable loss of the adsorbent.

Thus, the research has been active to find alternative and yet efficient sorbents. These adsorbents should have the following properties: the ability to reduce the concentration of pollutants below the acceptable limits, high adsorption capacity and long lifetime. Biosorbents, which are sorbents of biological origin, have proved to be good sorbents for many different pollutants.

2.3 Biosorption

As early as in 1986, at a meeting organized by the Solvent Engineering Extraction and Ion Exchange Group of the Society of Chemical Industry at UK, biosorption was regarded as an emergent technology. Since then, a number of
centers all over the world have been engaged in the area of biosorption with precise goals of identifying potential biosorbents. Results of research during the last two decades showed that biosorption is an ideal alternative for decontamination of metal containing effluents (Gupta et al., 2000).

2.3.1 Biomass Sources

Three major sources of biomass can be readily identified:

1. Waste biomass from industrial large scale fermentations (e.g. from antibiotics, enzyme, organic acid production processes, etc.) (Chubar et al., 2004; Aksu and Yener, 2001; Aksu and Gonen 2004; Aksu and Akpinar, 2001). Basically, industrial biomass comes in the form of amorphous "mud" and requires different types of more or less sophisticated processing into granules of desirable physio-chemical properties before it could be considered as biosorbent (Volesky, 2003).

2. Microorganisms: A wide variety of microorganisms (both living and nonviable) have been found to be capable of sequestering trace levels of metal ions from dilute aqueous solutions. The nonviable forms have been proposed as potential sorbents, since these are essentially dead materials, which require no nutrition to maintain biomass. Problems associated with metallic toxicity in living biomass and the need to provide suitable growth media also do not arise. Indeed, many early studies have shown that nonliving biomass may be even more effective than living cells. One of the most promising types of biosorbents is marine algae biomass (seaweeds), in view of their high uptake capacity as well as the ready abundance of the biomass in many parts of the world's ocean (Sheng et al., 2004). Algae, bacteria, fungi, and yeasts have proved to be potential metal sorbents (Veglio and Beolchini, 1997). Many studies have demonstrated the efficiency of metals and organics removal by microbial biomass under a range of physical and chemical conditions (Rao and Viraraghavan, 2002; Denzili et al., 2004; Feng and Aldrich, 2004; Arica et al., 2004; Abu Al-Rub et al., 2004; Pagnanelli et al., 2001; Ibanez and Umetsu, 2004).
3. Agricultural wastes: Various agricultural products and by-products have been investigated to remove dyes from aqueous solutions. These include cotton waste, rice husk, bark (Mckay et al., 1999), sugar industry mud (Magdy and Daifullah, 1998), peat (Ho et al., 2002), tree fern (Ho et al., 2005), olive pomace (Pagnanelli et al., 2003).

2.3.2 Biosorption Mechanisms

2.3.2.1 Ion Exchange

Ion exchange is the interchange of ions which are formed by molecular or atomic species either losing or gaining electrons. The ion exchange properties of certain natural polysaccharides have been studied in detail and it is well established that bivalent metal ions exchange with counter-ions from active groups of polysaccharides such as alginic acid (ALG) (Volesky, 2003):

$$2NaALG + Me^{+2} \leftrightarrow Me(ALG)_2 + 2Na$$  \hspace{1cm} (2.1)

Relatively recently, it has been confirmed that ion exchange is predominantly involved in metal biosorption by algal biomass (Volesky, 2003).

2.3.3.2. Sorption

Adsorption is a process by which molecules adhere to solid surfaces. Note the fact that the definition implies no mechanical aspects of the nature of binding. The attraction may often be based on electrostatic charges. The term adsorption implies a surface phenomenon, the actual sequestration may take place based on either physical phenomena (physical adsorption) or through a variety of chemical binding means (chemisorption). The differences between chemisorption and physical adsorption are summarized in Table 2.1.
Table 2.1 Fundamentals of sorption methods (Volesky, 2003)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Physical Adsorption</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature Range</td>
<td>Lower</td>
<td>Higher</td>
</tr>
<tr>
<td>Heat of Adsorption</td>
<td>Lower</td>
<td>Higher</td>
</tr>
<tr>
<td>Order of H Condensation</td>
<td>Fast</td>
<td>Reaction</td>
</tr>
<tr>
<td>Activation Energy</td>
<td>Low E</td>
<td>Low E</td>
</tr>
<tr>
<td>Coverage</td>
<td>Multilayer possible</td>
<td>Monolayer</td>
</tr>
<tr>
<td>Reversibility</td>
<td>High</td>
<td>Often irreversible</td>
</tr>
</tbody>
</table>

2.3.2.3. Inorganic Microprecipitation

Microprecipitation of metals results when the solubility of the sorbate reaches its limit. When biosorption is studied, special attention should be paid that the solubility limits are not exceeded even locally because the consequence would be that the metal is not removed from solution by sorption but by precipitation.

2.4 Biosorption by Immobilized Cells

Cell immobilization is an attractive technique to fix and retain biomass on suitable natural or synthetic materials support for a range of physical and biochemical unit operations (Abu Al. Rub et al., 2004). Immobilization of the biomass in solid structures creates a material with the right size, mechanical strength, rigidity and porosity necessary for use in unit operations typical of chemical engineering (Veglio and Beolchini, 1997).
The main advantages of this technique include:

- Improved biomass performance and biosorption capacity (Akşu and Gonen, 2004).
- Increase mechanical strength (Aksu and Gonen, 2004).
- Facilitate separation of biomass from pollutant bearing solution (Aksu and Gonen, 2004).
- Immobilization can overcome processing problems arising from using powder biomass which in most cases has low density and strength (Abu Al. Rub et al., 2004).
Chapter: 3

Isothermal Modelling

3.1 Sorption Equilibrium

Sorption processes involve a solid phase (sorbent) and either a liquid phase containing a dissolved species to be sorbed or gas phase which contains some gases to be sorbed. Due to the higher affinity of the sorbent for the sorbate species the latter is attracted into the solid and bound there by different mechanisms. This process takes place until equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases.

The efficiency of the sorbent material is determined based on the amount of sorbate it can attract and retain in an immobilized form. This is usually expressed by sorbate uptake which determines the amount of sorbate removed from the solution per unit mass of the sorbent. It can be calculated by carrying out material balance on the sorbate. The difference between the initial amount of the sorbate in solution and its final amount will be the amount of sorbate bound to the sorbent. Thus, sorbate uptake, \( Q \) (mg/g), is given by the equation:

\[
Q = \frac{V (C_i - C_e)}{w}
\]  

(3.1)

Where \( V \) (L) is the volume of the sorbate-bearing solution contacted (batch) with the sorbent; \( C_i \) and \( C_e \) (mg/L) are the initial and equilibrium concentrations of the sorbate in the solution, respectively, and \( w \) (g) is the mass of sorbent.

3.2 Equilibrium Isotherm Equations

Equilibrium isotherm equations are used to describe experimental sorption data. The equation parameters and the underlying thermodynamic assumptions of these
equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinity of the sorbent (Ho et al., 2002).

### 3.2.1 Langmuir Isotherm

Langmuir (1918) was the first to propose a coherent theory of adsorption of gases onto a flat surface based on a kinetic viewpoint, that is there is a continual process of bombardment of molecules onto the surface and a corresponding evaporation (desorption) of molecules from the surface to maintain zero rate of accumulation at the surface at equilibrium (Do, 1998). Currently, it is one of the most commonly used models to describe gas and liquid adsorption processes. The assumptions of the Langmuir model are: (1) surface is homogeneous, that is adsorption energy is constant over all sites, (2) adsorption on surface is localized, that is adsorbed atoms or molecules are adsorbed at definite, localized sites, and (3) each site can accommodate only one molecule or atom. Based on these assumptions, the Langmuir isotherm was derived to give the equation

\[ Q = \frac{Q_{\text{max}} b C_e}{1 + b C_e} \quad (3.2) \]

Where \( Q_{\text{max}} \) is the maximum sorbate uptake under the given conditions, \( b \) is a coefficient related to the affinity between the sorbent and sorbate (=1/K where K is the affinity constant) and it is related to the energy of adsorption through Arrhenius equation. The higher \( b \) (smaller K), the higher is the affinity of the sorbent for the sorbate. The affinity of the sorbent to the sorbate at different sorbate concentrations can be predicted using the constant \( b \) and a dimensionless separation factor, \( R_L \) (Abu Al Rub et al., 2004).

\[ R_L = \frac{1}{1 + b C_o} \quad (3.3) \]

The criteria shown in Table 3.1 indicate the favorability of sorbate on Sorbent.
Table 3.1 Characteristics of Adsorption Langmuir Isotherm

(Abu Al-Rub et al., 2004).

<table>
<thead>
<tr>
<th>Separation Factor</th>
<th>Characteristics of Adsorption Langmuir Isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_L &gt; 1$</td>
<td>Unfavorable</td>
</tr>
<tr>
<td>$R_L = 1$</td>
<td>Linear</td>
</tr>
<tr>
<td>$0 &lt; R_L &lt; 1$</td>
<td>Favorable</td>
</tr>
<tr>
<td>$R_L = 0$</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

The Langmuir model has eventually been empirically most often used since it contains the two useful and easily imaginable parameters ($Q_{\text{max}}$ and $b$) which are more easily understandable since they reflect the two important characteristics of the sorption system (Voileskey, 2003).

3.2.2 Freundlich Isotherm

The Freundlich equation is one of the earliest empirical equations used to describe equilibria data. It does not indicate a finite uptake capacity of the sorbent and can thus be reasonably applied in the low to intermediate concentrations ranges.

The Freundlich isotherm model is given by the equation:

$$Q_e = K C_e^{(1/n)} \quad (3.4)$$

Where $K$ and $n$ are the Freundlich constants which represent sorption capacity and sorption intensity, respectively.

3.2.3 Dubinin-Radushkevich (D-R)

This isotherm is generally expressed as follows (Dubinin, 1960):

$$Q_e = Q_{D} \exp(-B_D [RT \ln (1+1/C_e)]^2) \quad (3.5)$$
Radushkevich (1949) and Dubinin (1965) have reported that the characteristic sorption curve is related to the porous structure of the sorbent. The constant, $B_D$, is related to the mean free energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution and this energy can be computed using the following relationship (Ho et al., 2002):

$$E = \frac{1}{\sqrt{2B_D}} \quad (3.6)$$

### 3.3 Determination of Isotherm Parameters by Linearization

The above mentioned parameters can be determined either by linearization or by non-linear regression techniques. Table 3.2 summarizes the linear forms that can be used to determine these parameters.

Table: 3.2 Isotherm constants for two parameter models by linear regression (Ho et al., 2002).

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Transformed</th>
<th>Slope</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X-values</td>
<td>Y-values</td>
<td></td>
</tr>
<tr>
<td>Langmuir</td>
<td>$C_e$</td>
<td>$C_e/Q_e$</td>
<td>$1/Q_e b$</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$\ln(C_e)$</td>
<td>$\ln(Q_e)$</td>
<td>$1/n$</td>
</tr>
<tr>
<td>Dubinin-Radushkevich</td>
<td>$(\ln(1+1/C_e))^2$</td>
<td>$\ln(Q_e)$</td>
<td>$-B_D R^2 T^2$</td>
</tr>
</tbody>
</table>
3.4 Determination of Isotherm Parameters by Non-Linear Regression

Due to the inherent bias resulting from linearization, alternative isotherm parameters were determined by non-linear regression. This provides a mathematically rigorous method for determining isotherm parameters using the original form of the isotherm equation (Ho et al., 2002).

In this study, four non-linear error functions were examined and the one with minimum error was selected for determining the isotherm parameters. The objective functions employed were:

1. The Sum of the Squares of the Errors (ERRSQ):

\[ \sum_{i=1}^{p} \left( Q_{e,\text{exp}} - Q_{e,\text{cal}} \right)^2 \]  

(3.7)

2. A Composite Fractional Error Function (HYBRD):

\[ \sum_{i=1}^{p} \left[ \frac{(Q_{e,\text{exp}} - Q_{e,\text{cal}})^2}{Q_{e,\text{exp}}} \right] \]  

(3.8)

3. A Derivative of Marquardt's Percent Standard Deviation (MPSD) (Marquardt, 1963):

\[ \sum_{i=1}^{p} \left( \frac{Q_{e,\text{exp}} - Q_{e,\text{cal}}}{Q_{e,\text{exp}}} \right)^2 \]  

(3.9)

4. The Average Relative Error (ARE) (Kapoor and Yang, 1989):

\[ \sum_{i=1}^{p} \left| \frac{Q_{e,\text{exp}} - Q_{e,\text{cal}}}{Q_{e,\text{exp}}} \right| \]  

(3.10)
Chapter: 4

Experimental

4.1 Chemicals

The stock solution of 1000 ppm zinc used in this study was prepared using analytical reagent grade of ZnSO₄·7H₂O (BDH, UK) in deionized water. The stock solution of 1000 ppm phenol was prepared with 1.25 g of 80% w/v phenol which is equivalent to 1 g of pure phenol liquid. The stock solution of 30 ppm naphthalene was prepared with 1.0 g of powdered naphthalene (Merck) in a 2 liters conical flask that was completed with deionized water. The stock solution was mixed and stirred for 24 h to achieve the maximum solubility value of naphthalene in water. 0.1N of Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the initial pH of the solution.

4.2 Preparation of Biosorbent

Immobilized algal cells were prepared by entrapping powdered *Chlorella vulgaris* cells, green algae (Watershed, USA) in an alginate matrix produced by ionic polymerization in calcium chloride solution, according to the following procedures (Abu Al Rub et al., 2004): the powdered algal cells were suspended in a 2% sodium alginate (BDH, UK) solution kept at a temperature of 60°C. The mixture was then dropped into a 2% calcium chloride (BDH, UK) solution using a peristaltic pump. The drops of Na-alginate solution gelled into 3.5±0.1 mm diameter beads upon contact with calcium chloride solution (Figure 4.1). The beads were washed well and then rinsed in deionized water and stored at 4°C.

For blank alginate beads, similar procedures were followed, but without algae (Figure 4.2).
4.3 Determination of Functional Groups

The functional acidic groups on the prepared algal cells were determined using Boehm's titration method (Abdulkarim and Abu Al Rub, 2004; Strelko et al., 2002): one g of the powdered algal cells was dispersed in 50 ml deionized water. The suspension was mixed with 0.1N solutions of sodium bicarbonate, sodium carbonate, and sodium hydroxide, and then shaken for 48 h at room temperature. After this time, the sample was left for 6 h so that particles can settle. The sample was then filtered and 10 ml of filtrate were titrated with 0.1 N volumetric HCl standard using a methyl red as the indicator. According to Boehm's titration method, sodium bicarbonate can neutralize carboxyl groups, sodium carbonate can neutralize carboxyl, lactones and lactols groups, and sodium hydroxide can neutralize carboxyl, lactones, lactols and phenols groups. Table (4.1) lists the different functional groups available on algal cells.

Table 4.1 The Functional Groups on the Algal Cells

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Meq H⁺/g algae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxyl</td>
<td>0.02</td>
</tr>
<tr>
<td>Lactones and Lactols</td>
<td>0.01</td>
</tr>
<tr>
<td>Phenols</td>
<td>0.035</td>
</tr>
</tbody>
</table>
Figure 4.1 immobilized algal beads prepared

Figure 4.2 White transparent alginate beads prepared
4.4 Procedure

4.4.1 Equilibrium Adsorption Isotherm

All experiments were conducted by adding a proper amount of beads into 100 ml reagent bottles containing 50 ml of the zinc, phenol, or naphthalene solution. Different initial concentrations were used: for zinc (20-350 ppm), for phenol (20-350 ppm) and for naphthalene (5-30 ppm). The mixtures in these bottles were agitated for a predetermined time in a shaker at 25°C. The zinc solution, then, was separated from sorbent and the concentration of zinc ions was determined using a Varian atomic absorption spectrophotometer. For phenol and naphthalene, similar procedures were followed but the concentrations were determined using UV spectrophotometer at wavelength of 270 nm for phenol and 273 nm for naphthalene.

The uptake, which represents the amount sorbate sorbed per unit mass of sorbent is calculated using the following equation:

\[ Q_e = (C_o - C_e) \frac{V}{w} \quad (4.3.1) \]

Where \( Q_e \) is the uptake (mg/g) at equilibrium, \( C_o \) the initial concentration sorbate (mg/ml), \( C_e \) the concentration at equilibrium (mg/ml), \( V \) the initial volume of solution, and \( w \) is the mass of sorbent (g).

4.4.2 Adsorption Kinetics

The kinetic studies were carried out by conducting batch biosorption experiments with 100 ppm of zinc at pH 5.0, 50 ppm of phenol at pH 11.0, and 24 ppm of naphthalene at pH 4.0. Samples were taken at different time periods and analyzed for the three species concentrations.

4.4.3 Competitive Biosorption

The competitive biosorption of zinc, phenol or naphthalene with nickel, copper, NaCl, and citric acid have been investigated. The studies involved
experiments with constant zinc, phenol or naphthalene concentration and varying other metals and chelating agents concentrations (50 – 250 ppm). The effect of naphthalene on phenol has been investigated at pH 11.0, and the effect of phenol has also been investigated but at pH 4.0. All the experiments have been conducted at 25°C using the same procedures used in the single adsorption experiments, and were carried out in triplicate.

4.5 Analytical Instruments

- pH meter (Thermo Orion, 420) has been used for pH determination of the zinc, phenol, and naphthalene solutions.
- UV Spectroscopy (PU 8630 UV/VIS/NIR Single Beam): the concentration of phenol and naphthalene has been measured by UV spectroscopy at wavelength ($\lambda = 270$ nm) and ($\lambda = 273$ nm) respectively.
- HPLC (Waters, Alliance 2695 separation module with column oven, detector: 2996 PDA, flow rate: 1.5 ml/min) has been used to measure the concentration of both phenol and naphthalene in deionized water sample.
- Varian Atomic Absorption (Spectra AA, 880) spectrophotometer has been used to measure the concentration of zinc.
Chapter: 5

Results and Discussion of Zinc

The results of zinc biosorption on dead algal cells are discussed in this chapter. At the beginning of this study a comparison between immobilized inactive algae and suspension algae was performed. Figure 5.1 shows the biosorption of zinc on immobilized and free suspension algal cells. This figure depicts that immobilized inactive algae resulted in higher zinc uptake than the suspension algae. Similar results were obtained by Gad (2000), where immobilized biomass of *Rhodopseudoligosporus* was more effective than freely suspended biomass for Cd$^{2+}$ biosorption.

![Figure 5.1 Uptake of biosorption of zinc using suspended and immobilized inactive algae (initial zinc ions concentration = 100 ppm, pH = 5, mass of algae = 0.02g)](image)
5.1 Effect of pH on Zinc Biosorption

Heavy metals biosorption is highly pH dependent (Abu Al Rub et al., 2004). The effect of pH on zinc sorption capacity of the immobilized dead algal cells was studied at 100 ppm zinc initial concentration and 0.15 g of algal cell. Figure 5.2 demonstrates the variation of the uptake of zinc with pH. The uptake of zinc increases from 1.83 to 7.26 mg/g over a narrow pH range (3.0-5.0). No significant increase in zinc uptake at pH values above 5.0 was observed. Similar trend was obtained in previous studies (Martins et al., 2004; Mohapatra and Gupta, 2005; Ramos et al., 2002). Solution pH affects both cell surface metal binding sites and metal chemistry in water (Abu Al-Rub et al., 2005). At low pH values ion exchange reaction involving metals are in competition with the high concentrations of H⁺ in the solution. With increasing pH, more ligands, such as amino and carboxyl groups, on sorbent would be exposed and thus negative charges will result and attraction between these negative charges and the metals would increase the biosorption capacity on the cell surface. Another reason for increasing zinc removal is that the isoelectric point for algal biomass is at pH 3.0 (Abu Al-Rub et al., 2005). At pH values above zero-point charge, the algal cells would have negative net charge and the ionic state of ligands on algal cell surface will be such as to endorse reaction with zinc ions. Thus, electrostatic attraction between zinc and the negatively charged algal cells surface would occur which will enhance the biosorption above pH 3.0 (Abu Al-Rub et al., 2005).
Figure 5.2  Effect of pH on zinc uptake (initial zinc ions concentration = 100 ppm mass of algal cell = 0.15 g)

5.2 Dynamics of Zinc Biosorption

The variation in uptake of zinc with shaking time was studied using solutions of zinc with initial concentration of 100 ppm at pH 5.0 and 0.3 g of algal cell. The shaking time was varied from 3 to 180 min. Figure 5.3 reveals the variation of the uptake of zinc versus time for immobilized inactive algae and blank alginate. The maximum zinc uptake with either sorbent was reached after 60 min. Figure 5.3 also indicates that sorption of zinc involves two stages. In the first stage, sorption is rapid where approximately 90% of the maximum zinc uptake occurred within the first 30 min in both cases of blank alginate and immobilized algal cells. This rapid sorption indicates that passive surface sorption occurs on the algal cells or beads surface. The second stage is slow and may involve other adsorption mechanisms such as intraparticle diffusion. The advantage of such rapid sorption in practical applications is that smaller reactor volumes can be used (Abu al Rub et al., 2004).

In order to analyze the sorption of zinc on blank alginate beads, and immobilized algal cells, the Lagergren rate equation will be applied. Usually,
adsorption of heavy metals is analyzed using the Lagergren first order or pseudo-second order kinetics (Ho and McKay, 1998).

The Lagergren first order is based on adsorbent capacity and is given by

\[ \frac{dQ_t}{dt} = k_{1,\text{ads}} (Q_e - Q_t) \]  

(5.1)

where \( k_{1,\text{ads}} \) (l/min) is the sorption first order rate constant, \( Q_e \) is the equilibrium uptake and \( Q_t \) is uptake at any time \( t \). Equation 5.1 can be integrated with the boundary condition: \( Q_t = 0 \), at \( t = 0 \) to give

\[ \ln(Q_e - Q_t) = \ln Q_e - k_{1,\text{ads}} t \]  

(5.2)

Thus, if the sorption dynamics follows the Lagergren first order, then a plot of \( \ln(Q_e - Q_t) \) vs. \( t \) should result in a straight line. However, in many cases, the Lagergren-first order equation fits sorption kinetics over the first 20-30 min of the sorption process (Aksu, 2001). Figure 5.4 presents a plot of \( \ln (Q_e - Q_t) \) versus \( t \) for the sorption of zinc on blank alginate and immobilized algal cells. The kinetic parameters for the sorption of zinc are shown in Table 5.1. As can be noticed from Figure 5.4 and Table 5.1, the Lagergren first order equation cannot describe the kinetic of sorption of zinc on blank alginate and immobilized dead algal cell.

The pseudo-second order kinetics, suggested by Ho and McKay, 1999 and Ho, 2004, is also based on the sorption capacity of the sorbent and is given by

\[ \frac{dQ_t}{dt} = k_{2,\text{ads}} (Q_e - Q_t)^2 \]  

(5.3)

An integrated pseudo-second order rate law can be obtained from equation (5.3) for the boundary conditions \( t = 0 \) to \( t = t \) and \( Q_t = 0 \) to \( Q_t = Q_e \), and is given by:

\[ \frac{1}{(Q_e - Q_t)} = \frac{1}{Q_e} + kt \]  

(5.4)

Equation (5.4) can be rearranged to obtain a linear form:
\[
\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{Q_e^2 k}
\]  

(5.5)

Where \( Q_e \) is the amount of sorbate sorbed at equilibrium (mg g\(^{-1}\)); \( t \) is the reaction time (min); \( Q_t \) is the amount of sorbate sorbed at time \( t \) (mg g\(^{-1}\)); \( k \) is the equilibrium rate constant of pseudo-second order sorption (g mg\(^{-1}\) min\(^{-1}\)). Using the equation (5.5) by plotting \( t/Q_t \) versus \( t \) should result in a straight line with slope \( 1/Q_e \) and intercept \( 1/kQ_e^2 \), as shown in Figure 5.5. The values of sorption rate constant and the equilibrium uptake with the correlation coefficient are listed in Table 5.1. Results revealed in Figure 5.5 and Table 5.1 prove that the kinetics for the sorption of zinc on blank alginate beads and immobilized inactive algae are pseudo-second order kinetics.

![Figure 5.3 Effect of shaking time (initial zinc ions concentration = 100 ppm, pH = 5.0, mass of algal cell = 0.3 g)](image-url)
Figure 5.4  Kinetics of biosorption of zinc: first order (mass of algal cell = 0.3 g, initial zinc concentration = 100 ppm, T = 25°C, pH = 5.0)

Figure 5.5  Kinetics of biosorption of zinc: pseudo-second order kinetics (mass of algal cell = 0.3 g, initial zinc concentration = 100 ppm, T = 25°C, pH = 5.0)
Table 5.1  Kinetic parameters for the biosorption of zinc ions on immobilized dead algal cells and blank alginate beads.

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>First order</th>
<th></th>
<th></th>
<th>Pseudo-second order</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_{1,ads}$</td>
<td>$Q_e$</td>
<td>$R^2$</td>
<td>$k_{2,ads}$</td>
<td>$Q_e$</td>
<td>$R^2$</td>
</tr>
<tr>
<td></td>
<td>(l/min)</td>
<td>(mg/g)</td>
<td></td>
<td>(g/mg.min)</td>
<td>(mg/g)</td>
<td></td>
</tr>
<tr>
<td>Immobilized dead algal cells</td>
<td>$9\times10^{-5}$</td>
<td>8.04</td>
<td>0.544</td>
<td>0.012</td>
<td>11.02</td>
<td>0.9985</td>
</tr>
<tr>
<td>Blank alginate beads</td>
<td>0.0031</td>
<td>2.23</td>
<td>0.618</td>
<td>0.011</td>
<td>10.24</td>
<td>0.9981</td>
</tr>
</tbody>
</table>

The contribution of intraparticle diffusion mechanism can be tested by applying the Weber and Morris equation, 1963

$$Q_t = k_d t^{0.5} \quad (5.6)$$

Where $k_d$ is the rate constant of intraparticle diffusion. According to Weber and Morris equation for intraparticle diffusion mechanism, the plot of $Q_t$ vs. $t^{0.5}$ should be linear. Figure 5.6 shows the variation of $Q_t$ versus $t^{0.5}$ (Weber – Morris equation 5.6). For immobilized inactive algae and blank alginate beads the relationship is a straight line but doesn’t pass through the origin which indicates that the intraparticle diffusion is not the only mechanism involved in the biosorption of zinc on immobilized dead algal cell.
5.3 Biosorption Isotherm

Zinc ions biosorption capacities of blank alginate beads and immobilized dead algal cells are presented as a function of the equilibrium concentration of zinc ions and the results are shown in Figure 5.7. Figure 5.7 shows that the amount of Zn\(^{2+}\) ions sorbed per unit mass of the biosorbent increased with increasing initial concentration of zinc ions in the biosorption medium. Higher equilibrium concentration enhances the mass transfer driving force, thus increasing the uptake. In addition, increasing equilibrium metal ion concentrations increases the number of collisions between metal ions and sorbent, which enhances the sorption process (Abu Al Rub et al., 2004). From this Figure, the maximum biosorption capacity on the blank alginate beads was 8.58 mg/g and on immobilized dead algal cells was 9.38 mg/g. Table 5.2 compares the maximum sorption capacities obtained in this study with some other values reported in the
The sorption capacity of zinc using the immobilized dead algal cells *Chlorella vulgaris* is greater than that has been found using similar biosorbents.

Table 5.2 Adsorption capacity for Zn$^{+2}$ using different low cost adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption Capacity (mg/g) of Zn$^{+2}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste tea leaves</td>
<td>11.77</td>
<td>Tee and Khan, 1988</td>
</tr>
<tr>
<td>Moss (mixture)</td>
<td>9.87</td>
<td>Al-Asheh et al., 1997</td>
</tr>
<tr>
<td>Hazelnut shells</td>
<td>1.78</td>
<td>Cimino and Toscano, 2000</td>
</tr>
<tr>
<td>Peat</td>
<td>9.3</td>
<td>Mckay et al., 1998</td>
</tr>
<tr>
<td>Fungi</td>
<td>9.81</td>
<td>Puranik et al., 1999</td>
</tr>
<tr>
<td>Aquatic moss <em>Fontinalis antipyretica</em></td>
<td>15</td>
<td>Martins et al., 2004</td>
</tr>
<tr>
<td>Immobilized dead algal cells <em>Chlorella vulgaris</em></td>
<td>9.38</td>
<td>This study</td>
</tr>
</tbody>
</table>
It is known that the constituents of the cell wall of algae provide an array of ligands with a mosaic of functional groups capable of binding various metallic ions. Indeed, it has been shown that many metal-binding mechanisms are involved in the biosorption process; these include ion exchange, complexation, coordination, and microprecipitation (Sheng et al., 2004). In addition to these, immobilization enhances the contribution of physical sorption.

The equilibrium isotherms for the sorption of zinc were obtained in batch experiments using initial concentrations of 20 – 350 ppm. The solution pH and the mass of adsorbent were kept unchanged. In order to optimize the design of a biosorption system to remove metal ions, it is important to establish the most appropriate correlations for the equilibrium curves. Three isotherm equations have been examined in the present study, namely: Langmuir (equation 3.2), Freundlich (equation 3.4), and Dubinin-Radushkevich (equation 3.5).
The linear Freundlich isotherm plots for the sorption of the zinc onto both blank alginate beads and immobilized dead algal cells are presented in Figure 5.8. Table 5.3 shows the linear Freundlich sorption isotherm constants and the coefficients of determination ($R^2$). Examination of the plot and the $R^2$ values suggests that the Freundlich isotherm could describe the sorption of zinc on both sorbents. This is supported by the fact that algal cells have active sites with different energies, a key assumption in Freundlich isotherm model. The values of the Freundlich model parameters can be used to predict the affinity between the sorbate and sorbent. High values of these parameters indicate high adsorptive capacity. From Table 5.3 the magnitude of K and n for both sorbents suggests easy uptake with high sorptive capacity.

The Freundlich isotherm constants were also determined by the non-linear regression Marquadt’s PSD (MPSD) as shown in Table 5.4. The results demonstrate that the values of the K and n obtained by non linear regression are remarkably consistent and quite similar to the linear transform values from Table 5.4. The Derivative of Marquardt's Percent Standard Deviation (MPSD) parameters are closest to those obtained by linearization, typically within 4.6%, based on the sum of normalized errors. On this basis it would thus seem that the linear Freundlich model does give a reasonable approximation to the parameter set found by non-linear regression. The minimum error occurs for the constants determined using MPSD in the cases of immobilized dead algae and blank alginate beads.

The sorption data were analyzed according to the linear form of the Langmuir isotherm. The plots of specific sorption ($C_e/Q_e$) against the equilibrium concentration ($C_e$) for zinc are shown in Figure 5.9, and the isotherm constants $Q_m$, $b$, and $R^2$ are presented in Table 5.3. The $R^2$ values suggest that the Langmuir isotherm provides a good model of the sorption system. The sorption equilibrium constant of the Langmuir model $b$, provides a measure for the adsorption efficiency since it indicates the sorbent affinity at low concentrations, and hence it measures the initial gradient of the adsorption isotherm. Higher values of $b$ indicate higher affinity and thus higher sorption efficiency. The affinity can also be tested using the Langmuir parameter $b$, to calculate the dimensionless
separation factor, $R_L$ (equation 3.3), defined by Hall et al., 1966. The values of $R_L$ for the sorption of zinc on blank alginate beads and immobilized dead algal cells as a function of initial concentration are shown in Figure 5.10. Considering the criteria shown in Table 5.3, the results indicate that the sorption of zinc on the studied sorbents is favorable at higher concentrations.

The results of using the non-linear error analysis are shown in Table 5.4, where they show that the Langmuir isotherm constants are very consistent among all methods and they were very close to those obtained using linear analysis.

Another less commonly used model to describe the sorption is the Dubinin-Radushkevich (D-R) isotherm (Figure 5.11). The values of $E$ calculated using equation (3.6) are 14.35 kJ/mole and 14.85 kJ/mole for blank alginate beads and immobilized dead algal, respectively. These values are within the range of ion-exchange mechanisms (8-16 kJ/mole), confirming that the ion exchange mechanism play a significant role in the biosorption mechanism. This finding of ion exchange mechanism contribution agrees with the suggested mechanism of biosorption proposed by Volešky (2003). The $Q_D$ values are consistent with the linear $Q_m$ values previously determined for the Langmuir isotherm.
Figure 5.8  Freundlich isotherms of zinc ions sorbed on different sorbents (mass of algal cell = 0.3 g, pH = 5.0)

Figure 5.9  Langmuir isotherms of zinc ions sorbed on different sorbents (mass of algal cell = 0.3 g, pH = 5.0)
Figure 5.10 "Separation" factor of zinc ions sorbed on different sorbents
(mass of algal cell = 0.3 g, pH = 5.0)

Figure 5.11 Dubinin-Radushkevich equation isotherm of zinc ion sorbed on
different sorbents (mass of algal cell = 0.3 g, pH = 5.0)
Table 5.3 Adsorption linear Isotherms parameters for the sorption of zinc ions by blank alginate beads and immobilized algal cells.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Blank alginate beads</th>
<th>Immobilized algal cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>K (l/mg)^n/mg/g</td>
<td>2.85</td>
<td>3.26</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>5.01</td>
<td>5.15</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.95</td>
<td>0.96</td>
</tr>
<tr>
<td>Langmuir</td>
<td>Q_m (mg/g)</td>
<td>9.25</td>
<td>9.67</td>
</tr>
<tr>
<td></td>
<td>b (l/mg)</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>D-R</td>
<td>Q_D (mmol/g)</td>
<td>8.83</td>
<td>9.44</td>
</tr>
<tr>
<td></td>
<td>B_D (l/l^2.mol^2)</td>
<td>2.01*10^-9</td>
<td>2*10^-9</td>
</tr>
<tr>
<td></td>
<td>E (kJ/mole)</td>
<td>14.35</td>
<td>14.85</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.97</td>
<td>0.98</td>
</tr>
</tbody>
</table>
Table 5.4  Adsorption non-linear Isotherms parameters for the sorption of zinc ions by blank alginate beads and immobilized algal cells.

<table>
<thead>
<tr>
<th>Model</th>
<th>Blank Alginate Beads</th>
<th>Immobilized Algal Cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich: K (l/mg)$^{1/3}$ (mg/g)</td>
<td>2.94</td>
<td>3.58</td>
</tr>
<tr>
<td>Freundlich n</td>
<td>5.27</td>
<td>5.86</td>
</tr>
<tr>
<td>Marquadt's PSD</td>
<td>0.031</td>
<td>0.12</td>
</tr>
<tr>
<td>Langmuir Q_m (mg/g)</td>
<td>8.37</td>
<td>8.83</td>
</tr>
<tr>
<td>Langmuir b (l/mg)</td>
<td>0.087</td>
<td>0.18</td>
</tr>
<tr>
<td>EAR</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>ERRSQ</td>
<td>0.96</td>
<td>0.96</td>
</tr>
</tbody>
</table>

5.4 Sorption/Desorption of Zinc

Sorption and desorption of zinc on immobilized dead algal cells and blank alginate beads was investigated by conducting three cycles of sorption/desorption experiments. Desorption of zinc was achieved by shaking the sorbents: the blank alginate beads or immobilized dead algal cells, in 20 ml 0.1 M of HCl for two hours. The sorbents were then rinsed with deionized water to remove any residual acidity. These sorbents were then used in the removal of zinc ions and the results are demonstrated in Figure 5.12. As can be seen in the Figure, zinc uptake was improved after the first cycle. This improvement may be attributed to the fact that "regeneration" or desorption using acid could free up more active sites by removing some contaminants that might have been bound previously by the algal
cells. These results indicate that repeated removal of heavy metal can be achieved by immobilized algal cells.

Figure 5.12 Repeated uptake removal of zinc (initial zinc ions concentration = 100 ppm, pH = 5.0, mass of algal cell = 0.3 g)
5.5 Effect of Impurities on Biosorption of Zinc

Industrial wastewaters contain in addition to heavy metals other organic and inorganic compounds, such as salts and chelating agents. The presence of these compounds is expected to affect the uptake of heavy metals. Figure 5.13 demonstrates the variation of zinc uptake versus equilibrium concentrations of zinc in the presence of Cu$^{2+}$, Ni$^{2+}$, NaCl or citric acid. The presence of any of these compounds affected the zinc uptake. The presence of other heavy metal ions (Cu$^{2+}$, Ni$^{2+}$) decreased the biosorption capacity of the immobilized dead algal cells. Many of the functional groups present on the algal cell wall and different cations compete for the binding sites. NaCl decreased the uptake insignificantly, since the presence of salt may results in a competition on the sorbent binding sites between metals and cations from the salts. Similar results were obtained using different sorbents (Jalali-Rad et al., 2004; Abdulkarim and Abu Al Rub, 2004). The uptake of zinc decreased in the presence of citric acid and this is expected since the presence of chelating agents in a solution in containing zinc is believed to form a complex between the zinc and the chelating agent. This complex changes the equilibrium pH of solution, which will decrease the uptake. These results were in agreement with other studies using different adsorbent and/or different heavy metals (Abu Al Rub, 2004; Juang et al., 1999).
Figure 5.13  Effect of impurities on zinc uptake on immobilized dead algal cells (mass of algal cell = 0.3 g, initial zinc concentration = 100 ppm, T = 25°C, pH 5.0, initial impurities concentrations = 100 ppm)
Chapter 6

Results and Discussion of Phenol and Naphthalene

Naphthalene and phenol are representative of highly toxic materials. These materials are carcinogen and represent two families of component that are existing in refining wastewater. The results of experiments conducted on biosorption on immobilized inactive algae and suspension algae are shown in Figures 6.1 and 6.2. These results show that immobilized inactive algae gave higher uptake removal than the suspension algae. A similar finding was found for biosorption of zinc as presented in chapter 5.

![Graph showing biosorption of phenol](image)

Figure 6.1 Uptake of biosorption of phenol using suspended and immobilized inactive algae (pH = 11, initial phenol concentration = 50 ppm, mass of algae = 0.0016 g)
6.1 Effect of pH on the Biosorption of Phenol and Naphthalene

The pH adsorption medium is one of the most effective parameters in the treatment of phenol and naphthalene by immobilized dead algal cell. It is related to the biosorption mechanisms onto the cell surfaces from water and reflects the nature of the physio-chemical interaction of species in solution and the cell adsorptive sites. Different species may have different pH optima, possibly due to the different solution chemistry of the species (Aksu and Akpinar, 2001). The medium pH affects the solubility of phenol or naphthalene and the ionization state of the functional groups (carboxyl, phenol, lactones) of the immobilized algal cell wall. The effect of pH on uptake of phenol and naphthalene is shown in Figures 6.3 and 6.4, respectively. Figure 6.3 shows that the uptake of phenol remained constant over pH range 2.0-6.0, and then increased as pH increased (6-11), similar results were reported by Denzili et al. (2004). The interaction forces between phenol and biomass are rather weak in acidic solutions. In acidic medium the phenol molecules get protonated and subsequently positively charged. This causes repulsion between the positively charged algal cell surface and phenol molecules leading to a
decreased uptake of phenol, and a positively charged surface site on the adsorbent does not favour the adsorption of phenol due to the electrostatic repulsion (Rao and Viraraghavan, 2002; Dabrowski et al., 2005; Aksu and Akpinar, 2001; Haghseresht et al., 2003). At pH values higher than 9.0, phenol is expected to become negatively charged phenoxide (Morrison and Boyd, 1992; Rao and Viraraghavan, 2002) thus ion and chemical binding between functional groups and the phenoxide ion is enhanced.

Figure 6.4 shows the uptake of naphthalene as a function of pH. This figure shows that the optimum pH was 4.0. This is due to the fact that at pH below 4.0, the overall surface charge on the cell is becomes positive (Liu and Pinto, 1997), which introduces additional protons in the solution which compete for carboxyl and carbonyl sites, thus the adsorption is expected to be reduced at low pH. The increase in uptake at higher pH is due to the nature of the specific interaction between naphthalene and the surface of algal cell; the aromatic solutes adsorb onto algal cell by electrostatic interactions (Dabrowski et al., 2005), weak attraction (Van der Waals forces) between naphthalene aromatic ring and carbon-oxygen complex on algal cell.
Figure 6.3  Variation of uptake of phenol versus pH (initial phenol concentration = 50 ppm, mass of algal cell = 0.15 g)

Figure 6.4  Variation of uptake of naphthalene versus pH (initial naphthalene concentration = 24 ppm, mass of algal cell = 0.15 g)
6.2 Dynamics of Phenol and Naphthalene Biosorption

The effect of contact time on the biosorption of phenol and naphthalene on immobilized dead algal cell and blank alginate beads was investigated by determining the uptake of phenol and naphthalene at different time intervals (3 – 120 min) using 0.024 and 0.3 g of algal cell respectively. Figures 6.5 and 6.6 depict the variation of uptake of phenol and naphthalene respectively versus time. Figure 6.5 shows that in the first 10 minutes, the uptake of phenol increased rapidly and linearly with increasing time where about 90% of the phenol removed occurred in this time, similar to the effect of biosorbent dose presented previously. Through the whole range of studied time, the uptake using immobilized inactive algae was greater than the uptake using blank alginate beads. The same trend was obtained for biosorption of zinc presented in chapter 5.

Figure 6.6 reveals similar trend in the case of biosorption of naphthalene. Similar results were obtained by Antizar-Ladislao and Galil (2004), for the biosorption of phenol and chlorophenols by acclimated residential biomass. However, to ensure adequate equilibrium time, the experiment were run for 60 min.

The Lagergren pseudo-first order (equation 5.1) and pseudo-second order (equation 5.3) kinetics are used to analyze the biosorption kinetics in this chapter. Figures 6.7 and 6.8 show fitting the sorption dynamics of 50 ppm phenol and 24 ppm naphthalene, respectively, and the results of fittings are summarized in Table 6.1. Figure 6.7 demonstrates the biosorption kinetic for phenol using first order equation 5.1. It is clearly proved from the fitting results shown in the Figure 6.7 that the Lagergren first order equation cannot describe the kinetic biosorption for phenol or naphthalene.

The kinetic biosorption for phenol and naphthalene were examined using pseudo-second order equation 5.3. Figure 6.9 and 6.10 reveal the variation of $t/Q_i$ versus time and the kinetic parameters for equation 5.3 are displayed in Table 6.1. The relationship between $t/Q_i$ and $t$ for phenol and naphthalene are found to be linear with $R^2$ value for the pseudo-second order for phenol and naphthalene of
0.99. These results proved that the dynamic biosorption for phenol and naphthalene are pseudo-second order kinetic (equation 5.3).

Weber and Morris (1963) reported that if particle diffusion is involved in the sorption process then a plot of uptake versus the square root of time results a linear relationship and that particle diffusion would be the rate controlling step if this line passes through the origin. As elucidated in Figures 6.11 and 6.12 for phenol and naphthalene respectively, the results show that the linear relationship holds well for phenol and naphthalene the results can be represented by such a linear relationship but they do not pass through the origin. This indicates that particle diffusion is involved in the sorption process but it is not the only rate-limiting mechanism and that some other mechanisms are involved.

Figure 6.5  Variation of uptake of phenol versus time (initial phenol concentration = 50 ppm, pH = 11.0, mass of algal cell = 0.024 g)
Figure 6.6 Variation of uptake of naphthalene versus time (initial naphthalene concentration = 24 ppm, pH = 4.0, mass of algal cell = 0.3 g)

Figure 6.7 Kinetics of biosorption of phenol: first order (mass of algal cell = 0.024 g, initial phenol concentration = 50 ppm, T = 25°C, pH = 11.0)
Figure 6.8  Kinetics of biosorption of naphthalene: first order (mass of algal cell = 0.3 g, initial phenol concentration = 24 ppm, T = 25°C, pH = 4.0)

Figure 6.9  Kinetics of biosorption of phenol: pseudo-second order kinetics (mass of algal cell = 0.024 g, initial phenol concentration = 50 ppm, T = 25°C, pH =11.0)
Figure 6.10 Kinetics of biosorption of naphthalene: pseudo-second order kinetics (mass of algal cell = 0.3 g, initial phenol concentration = 24 ppm, T= 25°C, pH = 4.0)
Table 6.1  Kinetic parameters for the biosorption of phenol and naphthalene on immobilized dead algal cells and blank alginate beads.

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Biosorbents</th>
<th>First order</th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_{1,ads}$ (l/min)</td>
<td>$Q_e$ (mg/g)</td>
</tr>
<tr>
<td>Phenol</td>
<td>Immobilized dead algal cells</td>
<td>0.0077</td>
<td>2.01</td>
</tr>
<tr>
<td></td>
<td>Blank alginate beads</td>
<td>0.0099</td>
<td>1.95</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>Immobilized dead algal cells</td>
<td>$3 \times 10^{-5}$</td>
<td>5.18</td>
</tr>
<tr>
<td></td>
<td>Blank alginate beads</td>
<td>0.015</td>
<td>0.88</td>
</tr>
</tbody>
</table>
Figure 6.11 Application of Weber–Morris equation for the sorption of phenol

Figure 6.12 Application of Weber–Morris equation for the sorption of naphthalene
6.3 Biosorption Isotherm

The effect of equilibrium concentration of phenol or naphthalene on the biosorption capacities of blank alginate beads and immobilized dead algal cells are displayed in Figures 6.13 and 6.14, respectively. These figures show that uptake significantly increased with the equilibrium phenol and naphthalene concentration. The maximum sorption capacities of the blank alginate beads and immobilized dead algal cells for phenol were 28.2 and 34.2 mg/g, respectively at pH 11.0, and the maximum sorption capacities of the blank alginate beads and immobilized dead algal cells for naphthalene were 4.72 and 5.32 mg/g, respectively at pH 4.0. The equilibrium concentration provides an important driving force to overcome all mass transfer resistances of phenol and naphthalene between the aqueous and solid phases. Hence a higher equilibrium concentration of phenol and naphthalene enhances the sorption process (Aksu and Yener, 2001; Banat et al., 2000). The high sorption capacity of the immobilized dead algal cells was due to the highly active functional groups such as carboxyl. Different adsorbents with a wide range of adsorption capacities for phenolic compounds and naphthalene compounds have been studied (Table 6.2).

![Figure 6.13 Experimental isotherms of phenol sorbed on different sorbents](image)

Figure 6.13 Experimental isotherms of phenol sorbed on different sorbents

(pH = 11.0, mass of algal cell = 0.024g)
Figure 6.14  Experimental isotherms of naphthalene sorbed on different sorbents (pH = 4.0, mass of algal cell = 0.3g)

Table 6.2  Adsorption capacities for phenol and naphthalene using different adsorbents.

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>Adsorbent</th>
<th>Adsorption Capacity (mmol/g) of phenol</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>Microorganism</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Phanerochaete</em></td>
<td>1.23</td>
<td>Denzili et al., 2004</td>
</tr>
<tr>
<td></td>
<td><em>Chrysosporium</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Activated carbon</td>
<td>0.1</td>
<td>Dargaville et al., 1996</td>
</tr>
<tr>
<td></td>
<td>Immobilized dead algal</td>
<td></td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>cells <em>Chlorella vulgaris</em></td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>Kaolinite</td>
<td>1.28</td>
<td>Lee and Kim, 2002</td>
</tr>
<tr>
<td></td>
<td>Halloysite</td>
<td>1.73</td>
<td>Lee and Kim, 2002</td>
</tr>
<tr>
<td></td>
<td>Zeolite</td>
<td>0.17</td>
<td>Chang et al., 2004</td>
</tr>
<tr>
<td></td>
<td>Immobilized dead algal</td>
<td>0.041</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>cells <em>Chlorella vulgaris</em></td>
<td>0.041</td>
<td></td>
</tr>
</tbody>
</table>
The Langmuir (equation 3.2), Freundlich (equation 3.4), and Dubinin-Radushkevich (equation 3.5) will be used to describe the relationship between the amount of phenol and naphthalene and their equilibrium concentration in solutions.

The equilibrium isotherms for the sorption of phenol and naphthalene were obtained in batch experiments using initial concentrations of 20 – 350 ppm for phenol and 5 – 30 ppm for naphthalene. The solution pH and the mass of adsorbent were kept unchanged. In order to optimize the design of a biosorption system to remove phenol and naphthalene, it is important to establish the most appropriate correlations for the equilibrium curves.

The sorption data were analyzed according to the linear form of Langmuir isotherm and the linear plots are shown in Figures 6.15 and 6.16 for phenol and naphthalene, respectively, and the corresponding values of the model parameters are listed in Table 6.3. Examination of the data shows that the Langmuir isotherm provides an excellent fit for phenol since the correlation coefficient $R^2$ was 0.99 for blank alginate beads and immobilized dead algal cell, while for naphthalene $R^2$ was 0.96 for blank alginate beads and 0.97 for immobilized dead algal cell. It should be noticed that saturation was not attained in the case of naphthalene since due to solubility limitations, the maximum initial concentration of naphthalene obtained was 30 ppm.

The affinity can be tested using the Langmuir parameter $b$, to calculate the dimensionless separation factor, $R_L$ (equation 3.3), defined by Hall et al., 1966. The values of $R_L$ for the sorption of phenol and naphthalene on blank alginate beads and immobilized dead algal cells as a function of initial concentration are shown in Figures 6.17 and 6.18. As can be depicted, the separation factor values were less than unity, suggesting favorable sorption (Table 3.1) of phenol and naphthalene on both blank alginate beads and immobilized dead algal cells.

The values of the non-linear objective functions are shown in Table 6.4, the Langmuir isotherm constants found by the different objective functions are found to be consistent and close to those found by linear regression.
The linear Freundlich isotherm plots for the sorption of the phenol and naphthalene onto both blank alginate beads and immobilized dead algal cells are presented in Figures 6.19 and 6.20. The Freundlich isotherm constants $K$ and $n$ are indicators of adsorption capacity and adsorption intensity, respectively. The Freundlich constants are listed in Table 6.3. The fit of the Freundlich equation to the experimental data was good since $R^2$ for phenol was found to be 0.99 for immobilized dead algal cell and 0.94 for blank alginate beads, while for naphthalene the $R^2$ values were 0.98 for immobilized dead algal cell and 0.99 for blank alginate beads. As noted in Table 6.3, the values of $n$ were greater than unity, indicating that phenol and naphthalene exhibited increased adsorption on immobilized dead algal cell at higher concentration (Bembnowska et al., 2003).

The Freundlich isotherm constants were also determined by non-linear regression Marquardt’s Percent Standard Deviation (MPSD) and Composite Fractional Error Function (HYBRD) as shown in Table 6.4. The results demonstrate that the values of the $K$ and $n$ obtained by non-linear regression are remarkably consistent and quite similar to the linear transform values from Table 6.3. The minimum error occurs for the constants determined using Marquardt’s Percent Standard Deviation (MPSD) (equation 3.9) in the case of phenol for both immobilized dead algae and blank alginate beads, while the minimum error occurs for the constants determined using Composite Fractional Error Function (HYBRD) (equation 3.8) in the case of naphthalene for both immobilized dead algae and blank alginate beads.

The final isotherm model to be used is the Dubinin-Radushkevich (D-R) isotherm (Figures 6.21 and 6.23). The parameters of the D-R model for the experimental data together with the corresponding value of $R^2$ are also listed in Table 6.3. The magnitude of $E$ is useful for estimating the type of adsorption process. For phenol $E$ was found to be 28.8 kJ/mole for immobilized algal cells and 23 kJ/mole for blank alginate beads, which is bigger then the energy range of adsorption reactions, 8-16 kJ/mole (Ho et al., 2002), the type of adsorption of phenol on immobilized algal cells and blank alginate beads was chemical adsorption. Similar $E$ values were obtained for Cr(VI) adsorption by Oguz, 2005, and 1,1,2,2-Tetrachloroethane, Tetrachloroethylene by Bembnowska et al., 2003.
However, values of $E$ for naphthalene were found to be 9.05 kJ/mole for immobilized dead algal cell and 9.12 kJ for blank alginate beads. The range for $E$ values in ion-exchange mechanisms is 8-16 kJ/mole. Thus ion-exchange appears to have made contribution in the adsorption of naphthalene onto immobilized dead algal and blank alginate beads.

Figure 6.15  Langmuir isotherms of phenol sorbed on different sorbents (mass of algal cell = 0.024 g, pH = 11.0)
Figure 6.16  Langmuir isotherms of naphthalene sorbed on different sorbents (mass of algal cell = 0.3 g, pH = 4.0)

Figure 6.17  "Separation" factor of phenol sorbed on different sorbents (mass of algal cell = 0.024 g, pH = 11.0)
Figure 6.18 "Separation" factor of naphthalene sorbed on different sorbents (mass of algal cell = 0.3 g, pH = 4.0)

Figure 6.19 Freundlich isotherms of phenol sorbed on different sorbents (mass of algal cell = 0.024 g, pH = 11.0)
Figure 6.20  Freundlich isotherms of naphthalene sorbed on different sorbents (mass of algal cell = 0.3 g, pH = 4.0)

Figure 6.21  Dubinin-Radushkevich equation isotherm of phenol sorbed on different sorbents (mass of algal cell = 0.024 g, pH = 11.0)
Figure 6.22 Dubinin-Radushkevich equation isotherm of naphthalene sorbed on different sorbents (mass of algal cell = 0.3 g, pH = 4.0)
Table 6.3 Adsorption of linear isotherms parameters for the sorption of phenol and naphthalene by blank alginate beads and immobilized algal cells.

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>Model</th>
<th>Parameter</th>
<th>Blank alginate beads</th>
<th>Immobilized algal cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>Freundlich</td>
<td>K (l/mg)1/n (mg/g)</td>
<td>21.51</td>
<td>26.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>n</td>
<td>12.54</td>
<td>17.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R²</td>
<td>0.94</td>
<td>0.99</td>
</tr>
<tr>
<td>Langmuir</td>
<td></td>
<td>Qₘ (mg/g)</td>
<td>34.72</td>
<td>37.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b (l/mg)</td>
<td>0.11</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R²</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>D-R</td>
<td></td>
<td>Qₐ (mmol/g)</td>
<td>41.34</td>
<td>41.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bₐ (l/J².mol²)</td>
<td>9.44*10⁻¹⁰</td>
<td>6.02*10⁻¹⁰</td>
</tr>
<tr>
<td></td>
<td></td>
<td>E (kJ/mole)</td>
<td>23</td>
<td>28.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R²</td>
<td>0.95</td>
<td>0.98</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>Freundlich</td>
<td>K (l/mg)1/n (mg/g)</td>
<td>1.19</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>n</td>
<td>1.29</td>
<td>1.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R²</td>
<td>0.99</td>
<td>0.98</td>
</tr>
<tr>
<td>Langmuir</td>
<td></td>
<td>Qₘ (mg/g)</td>
<td>17.98</td>
<td>11.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b (l/mg)</td>
<td>0.061</td>
<td>0.13</td>
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<tr>
<td></td>
<td></td>
<td>R²</td>
<td>0.97</td>
<td>0.96</td>
</tr>
<tr>
<td>D-R</td>
<td></td>
<td>Qₐ (mmol/g)</td>
<td>2.37</td>
<td>2.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bₐ (l/J².mol²)</td>
<td>6.1*10⁻⁹</td>
<td>6.0*10⁻⁹</td>
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<tr>
<td></td>
<td></td>
<td>E (kJ/mole)</td>
<td>9.12</td>
<td>9.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R²</td>
<td>0.99</td>
<td>0.96</td>
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Table 6.4 Adsorption of non-linear isotherms parameters for the sorption phenol and naphthalene by blank alginate beads and immobilized algal cells.

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>Model</th>
<th>Blank Beads</th>
<th>Alginate Beads</th>
<th>Immobilized Cells</th>
<th>Algal Cells</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(l/mg)ln (mg/g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Freundlich n</td>
<td>12.08</td>
<td>19.10</td>
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<tr>
<td></td>
<td>Marquadt’s PSD</td>
<td>0.004</td>
<td>0.001</td>
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<tr>
<td></td>
<td>Langmuir Qm (mg/g)</td>
<td>33.41</td>
<td>35.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Langmuir b (l/mg)</td>
<td>0.23</td>
<td>0.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Marquadt’s PSD</td>
<td>0.016</td>
<td>0.009</td>
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<tr>
<td>Naphthalene</td>
<td>Freundlich: K</td>
<td>1.31</td>
<td>3.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(l/mg)ln (mg/g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Freundlich n</td>
<td>1.29</td>
<td>1.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HYBRD</td>
<td>0.19</td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Langmuir Qm (mg/g)</td>
<td>13.87</td>
<td>15.75</td>
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<tr>
<td></td>
<td>Langmuir b (l/mg)</td>
<td>0.10</td>
<td>0.074</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>HYBRD</td>
<td>0.1</td>
<td>0.05</td>
<td></td>
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</tr>
</tbody>
</table>
6.4 Effect of Impurities on Biosorption of Phenol and Naphthalene

The effect of the presence of Cu\(^{2+}\), Ni\(^{2+}\), NaCl and citric acid on phenol uptake. As shown in Figure 6.23, the uptake of phenol seems to be unaffected with the addition of metal ions (Ni\(^{2+}\) and Cu\(^{2+}\)), since at pH \(\geq 8\) the removal takes place by adsorption as well as precipitation i.e. the OH ions from the solution formed some complexes with Ni\(^{2+}\) and Cu\(^{2+}\) (Feng and Aldrich, 2004; Sheng et al., 2004; Ramos et al., 2002; Mohan and Singh, 2002). The uptake of phenol decreased in the presence of NaCl this is due to the competition between phenol and the chelating agents. While the uptake of phenol decreased in the presence of citric acid due to the decrease in pH.

The uptake of naphthalene seems to decrease with the addition of metals ions (Cu\(^{2+}\) and Ni\(^{2+}\)) and chelating agent (citric acid) (Figure 6.24). This decrease in the uptake is attributed to the competition of these compounds with naphthalene for the adsorption sites on the surface and that some sites might be occupied by the other component. As a consequence, the first component has a smaller "parking space" and its uptake is decreased (Aksu and Akpınar, 2001), similar results were obtained by Nollet et al., 2003, for the removal of organic materials by fly ash where the interference of ions lead to decrease in the uptake.
Figure 6.23  Effect of impurities on phenol uptake on immobilized dead algal cells (mass of algal cell = 0.024 g, initial phenol concentration = 50 ppm, T = 25°C, initial pH = 11.0, initial impurities concentrations = 100 ppm)

Figure 6.24  Effect of impurities on naphthalene uptake on immobilized dead algal cells (mass of algal cell = 0.3 g, initial naphthalene concentration = 24 ppm, T = 25°C, initial pH = 4.0, initial impurities concentrations = 100 ppm)
6.5 Interference in a Mixture of Phenol and Naphthalene

The interference in the mixture of phenol and naphthalene are studied and revealed on the previously mentioned Figures 6.13 and 6.14. The results shown in Figure 6.13, are those where the concentration of naphthalene was kept constant for a series of experimental runs, while phenol initial concentration was changed and the same has been applied for naphthalene and depicted in Figure 6.14.

Figure 6.13 shows that there is no significant effect of naphthalene on phenol at pH 11.0, and this is due to the fact that naphthalene has maximum adsorption at pH 4.0 in the acidic medium, this suggest that there is slight competition between phenol and naphthalene at high pH.

Moreover, the effect of phenol on naphthalene at pH 4 is shown in Figure 6.14, the uptake decreased from 4.72 to 3.17 mg/g, and this is due to the weak competition between phenol and naphthalene.
Conclusions and Recommendations

This study is an attempt to investigate the possibility of using immobilized inactive green algae to remove the main priority pollutants from refinery wastewater. These biosorbents are cheap and effective. The main findings of this study are:

- Sorption efficiency of immobilized biosorbents was greater than the suspension biosorption.
- The solution pH played a very important role for biosorption of the three pollutants and the optimum pH values were: 5.0 for zinc, 4.0 for naphthalene and 11.0 for phenol.
- Biosorption kinetics was found to follow pseudo-second order kinetics.
- Alginate beads and immobilized *Chlorella vulgaris* cells could be used in successive sorption/desorption cycles to remove zinc ions from aqueous solutions, which suggests that immobilization can provide an efficient and convenient method for repetition use of algal cells.
- Biosorption on alginate beads and immobilized *Chlorella vulgaris* have been found to follow Langmuir, Freundlich, and D-R isotherm models.
- The biosorption of zinc on immobilized algal cells and blank alginate beads is expected to be a result of combination of ion exchange, electrostatic interactions, intraparticle diffusion, and surface complexation mechanisms.
- The biosorption mechanism for phenol is chemisorptions and intraparticle diffusion. While for naphthalene, ion-exchange appears to have made contribution in the adsorption of naphthalene onto immobilized dead algal and blank alginate beads.
- The interference between phenol and naphthalene caused a slight decrease in the uptake.

The main recommendations are:

- Breakthrough curves studies need to be conducted.
الملخص

المعادن النقالة وتلوث المواد العضوي في النظام المائي أُصْبِحَ تهديد خطير اليوم، من هذه الملوثات البيئية المشتركة الخارجين والفينول والنفتالين. المصير ونقل هذه المواد الكيميائية يجب أن نفهم بما فيه الكفاية لتوقع تأثيرات بيئية ضارة وتطوير العمل العلاجي الملائم تقنياً واقتصادياً لتقليل مهنة بيئية. في هذه الدراسة، كتلة عضوية مكورية ظهرت كخيار لتطوير معالجة مياه الفيضلات الإقتصادية. كتلة الطحالب العضوية الميطة قد تُعْزَل المعادن بشكل سلبي ومواد عضوية بعملية الأدمتصاص من الحلول المخفقة، حيث كتلة عضوية تُشْتَغل كمبدل آيون استنادًا إلى مجموعات مختلفة تفاعلية متوفرة على سطح الخلية مثل الكاربوكسيل. هذه التقنية لها فوائد تشكيلة التشغيل المنخفضة.

الاستعمال المحتمل لحببيات الخالية من الطحالب وخلايا الطحالب المشلولة الميطة لإزالة الخارجين والفينول والنفتالين من الحلول المائية حُقِقْت فيها. لقد وُجِدَ أن الأدمتصاص الحيوي أثر بشكل ملحوظ بالرقم الهيدروجيني. الحركيّة وتجارب الأيسوثرمُ ثُقِدت في الرقم الهيدروجيني المثاليّة 5.0 و11.0 و4.0 للخارجين الفينول والنفتالين، على التوالي. نسبة إزالة الخارجين كانت سريعة وقصوى حدثت ضمن الثلاثون دقيقة الأولى في حبات الحبيبات الخالية من الطحالب وخلايا الظهاب المشلولة. من الناحية الأخرى، منفذ الموارنة لجزء ضمن الأول خمس دقائق في حالة الفينول والنفتالين. بيانات الموارنة لادمتصاص الحيوي لأيونات الخارجين والفينول والنفتالين في كلما الإمتصاص الحيوي يمكن أن يُلائم بشكل كافٍ من قبل Dubinin و Freundlich، Langmuir و Di آر) معادلات أيسوثرم. لقد وُجِدَ أيضاً في حضور Radushkevich.
معالجة الملوثات الأولوية
في المياه الملوثة الناتجة من مصافي البتروال بطريقة
الادمتصاص الحيوي

إعداد
دين عدنان شيخة

اطروحة مقدمة لعمادة الدراسات العليا
جامعة الإمارات العربية المتحدة
لاستكمال متطلبات درجة الماجستير في علوم موارد المياه

 مايو 2005