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**REMOVAL OF TRACE CONTAMINANTS FROM
WASTEWATER EFFLUENTS USING
LOCAL ADSORBENTS.**

BY

KASIM GHULAM HAIDER GHULAM

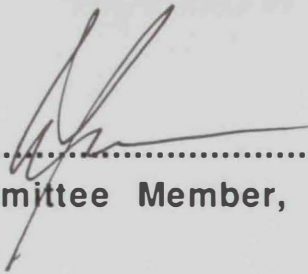
**A Thesis submitted to the Faculty of Science of the
United Arab Emirates University
in partial fulfillment of the requirements
for the degree of Master of Science
in
Environmental Science**

**Faculty of Science
United Arab Emirates University
(June, 1999)**


The thesis of Kasim Ghulam Haider Ghulam for the degree of Master of Science in Environmental Sciences is approved .



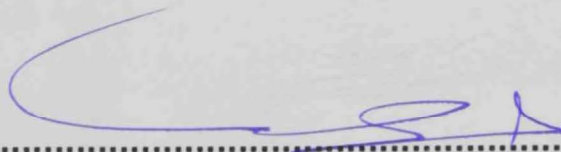
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ABSTRACT

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Wastewater reclamation must ensure removal of residual pollutants to a high degree so as to make the water acceptable for the designated reuse. There has been a growing interest worldwide to employ cost-effective treatment methods for polishing secondary treatment wastewater effluents. Carbon adsorption has proved to be an effective method for effluent polishing but treatment costs are relatively high.

Al-Ain wastewater treatment plant at Zakher has a design capacity of 54,000 m³/day and incorporates preliminary treatment, followed by extended aeration and dual-media filtration for effluent polishing before water reuse in irrigation. The chemical quality of the treated effluent produced at Zakher treatment plant has yet to be determined. Of primary importance are the trace organic contaminants (e.g. phenols) that adversely affect the effluent quality and suitability for reuse. After the chemical contaminants are quantitatively identified it is essential to determine adequate methods for further polishing of the effluent by utilizing locally available adsorbents. For this purpose, Palm Date Kernel Activated Carbon (PDKAC), a locally made adsorbent, has been used for the adsorption of compounds (phenol, aniline, and methylene blue) in batch tests at 25 °C and adsorbent particle size $\leq 75 \mu\text{m}$.

This must be investigated and the results of this study can be helpful in developing an economically viable method for removal of residual pollutants from wastewater effluents. If recommended water quality standards can be met, the treated water can be utilized for other municipal, industrial and agricultural purposes.

The removal of trace contaminants from wastewater effluent using local adsorbents has been investigated using adsorption techniques. The experimental results have indicated that the PDKAC has high selectivity for adsorbing phenol > aniline > methylene blue. The experimental isotherm data were fitted by both Freundlich and Langmuir isotherm models. The results revealed the potential use of PDKAC as a low-cost adsorbent.

TABLE OF CONTENTS

TABLE OF CONTENTS

| | PAGE |
|--|------|
| ACKNOWLEDGMENT | I |
| ABSTRACT | II |
| LIST OF FIGURES | VII |
| LIST OF TABLES | IX |
| LIST OF ABBREVIATIONS | X |
| | |
| CHAPTER 1: INTRODUCTION & PROBLEM DEVELOPMENT | |
| 1.1 General | 1 |
| 1.2 Objectives and Impact of the Study | 7 |
| 1.3 Tasks | 8 |
| 1.4 Thesis Organization | 9 |
| | |
| CHAPTER 2: LITRATURE REVIEW | |
| 2.1 Preparation of Active Carbon | 10 |
| 2.1.1 Preparation Techniques | 11 |
| 2.1.2 Types of Activated Carbon | 15 |
| 2.1.3 Activated Carbon Production | 18 |
| 2.2 Adsorption Mechanisms | 21 |
| 2.2.1 Activated Carbon Adsorption | 21 |
| 2.2.2 Adsorption from Solution | 25 |
| 2.3 Analysis of the Adsorption Process | 37 |
| 2.3.1 Freundlich Isotherm | 38 |
| 2.3.2 Langmuir Isotherm | 39 |

| | | |
|-------|--|----|
| 2.3.3 | Mass-Transfer Zone | 39 |
| 2.3.4 | Carbon Adsorption Capacity | 41 |
| 2.3.5 | Breakthrough Adsorption Capacity | 41 |
| 2.4 | Wastewater Treatment | 43 |
| 2.4.1 | Wastewater Composition (Pollutants) | 43 |
| 2.4.2 | Characteristics of Domestic Wastewater | 46 |
| 2.4.3 | Classification of Wastewater Treatment Methods | 48 |
| 2.4.4 | Wastewater Treatment Plant in Al Ain | 49 |

CHAPTER 3: MATERIAL & METHODS

| | | |
|-------|---|----|
| 3.1 | Material | 53 |
| 3.1.1 | Adsorbent | 53 |
| 3.1.2 | Adsorbate | 53 |
| 3.2 | Equipment | 54 |
| 3.3 | Methods | 54 |
| 3.3.1 | Preparation of Activated Carbon (Adsorbent) | 54 |
| 3.3.2 | Determination of Equilibrium Time | 55 |
| 3.3.3 | Adsorption Isotherms | 56 |

CHAPTER 4: RESULTS & DISCUSSIONS

| | | |
|-----|---|----|
| 4.1 | Physiochemical Properties of PDKAC adsorbent | 57 |
| 4.2 | Morphological Characterization of PDKAC Adsorbent | 58 |
| 4.3 | Infrared Analysis | 61 |
| 4.4 | Typical Analysis of Zakher Wastewater Treatment Plant | 62 |
| 4.5 | Physiochemical Properties of Adsorbate Solution | 63 |
| 4.6 | Equilibrium Time | 64 |
| 4.7 | Adsorption Isotherms | 65 |
| 4.8 | Analysis of Adsorption Isotherms | 68 |

| | |
|--------------------------------------|----|
| 4.8.1 Freundlich Isotherms | 68 |
| 4.8.2 Langmuir Isotherm | 72 |
| 4.8.3 Comparison of Models | 76 |
| 4.8.4 Possible Adsorption Mechanisms | 79 |

CHAPTER 5: SUMMARY & CONCLUSIONS

| | |
|----------------------------------|----|
| Summary & Conclusions | 83 |
| Recommendations for Future Study | 85 |

| | |
|-------------------|----|
| REFERENCES | 86 |
|-------------------|----|

| | |
|-----------------|----|
| APPENDIX | 90 |
|-----------------|----|

LIST OF FIGURES

LIST OF FIGURES

| | PAGE |
|---|-------------|
| Figure 4-1 Scanning electron microscope picture of palm date kernel (PDKAC) units (peds) and the macropores. | 58 |
| Figure 4-2 Scanning electron microscope picture of PDKAC unit showing pore sizes and their arrangements. | 59 |
| Figure 4-3 Scanning electron microscope picture of PDKAC particles and micropores. | 60 |
| Figure 4-4 Infrared spectrum of (PDKAC) | 61 |
| Figure 4-5 Adsorption rate of phenol at different times onto PDKAC at 25 °C | 64 |
| Figure 4.6 Adsorption isotherm for phenol onto (PDKAC) at 25 °C. | 65 |
| Figure 4.7 Adsorption isotherm for aniline onto PDKAC at 25 °C. | 66 |
| Figure 4.8 Adsorption isotherm for Methylene Blue onto PDKAC at 25 °C. | 67 |
| Figure 4-9 Freundlich isotherm for phenol at 25 °C | 69 |
| Figure 4-10 Freundlich isotherm for aniline at 25 °C | 70 |

| | |
|--|----|
| Figure 4-11 Freundlich isotherm for Methylene Blue at 25 °C | 71 |
| Figure 4-12 Langmuir isotherm for phenol at 25 °C | 73 |
| Figure 4-13 Langmuir isotherm for aniline at 25 °C | 74 |
| Figure 4-14 Langmuir isotherm for methylene blue at 25 °C | 75 |
| Figure 4-15 Comparison between predicted results from Freundlich & Langmuir models and experimental results for phenol. | 76 |
| Figure 4-16 Comparison between predicted results from Freundlich & Langmuir models and experimental results for aniline. | 77 |
| Figure 4-17 Comparison between predicted results from Freundlich & Langmuir models and experimental results for methylene blue. | 78 |
| Figure 4-18 The chemical structure of phenol | 80 |
| Figure 4-19 The chemical structure of aniline | 80 |
| Figure 4-20 The chemical structure of methylene blue | 80 |

LIST OF TABLES

LIST OF TABLES

| | PAGE |
|---|-------------|
| Table 2-1 World production of active carbon. | 19 |
| Table 2-2 Typical composition of untreated domestic wastewater. | 44 |
| Table 2-3 Types and numbers of microorganisms typically found in domestic wastewater. | 45 |
| Table 2-4 The classification and general specification of Zakher wastewater treatment plant. | 52 |
| Table 4-1 Physiochemical properties of locally-made PDKAC adsorbent. | 57 |
| Table 4-2 Characteristics of final effluent at Zakher wastewater treatment plant | 62 |
| Table 4-3 The physiochemical properties of phenol, aniline, and methylene blue | 63 |
| Table 4-4 Freundlich parameters for the adsorption of phenol, aniline, and methylene blue | 68 |
| Table 4-5 Langmuir parameters for the adsorption of phenol, aniline, and methylene blue | 73 |

LIST OF ABBREVIATIONS

LIST OF ABBREVIATIONS

| | |
|------------------|---|
| a | = Langmuir constant |
| AWT | = Advanced wastewater treatment |
| b | = Langmuir constant |
| BOD | = Biochemical oxygen demand |
| BOD ₅ | = Biochemical oxygen demand for 5 days |
| C ₀ | = Initial liquid-phase concentration (mg/l) |
| C _e | = Equilibrium liquid-phase concentration (mg/l) |
| °C | = Degree Centigrade |
| COD | = Chemical oxygen demand |
| DWF | = Dry weather flow |
| EPA | = Environmental protection agency |
| °F | = Degree Fahrenheit |
| g | = Gram |
| GAC | = Granular activated carbon |
| hr | = Hour |
| IAS | = Ideal adsorption solution |
| IR | = Infrared |
| k | = Parameter of Freundlich isotherm |
| °K | = Degree Kelvin |
| m ³ | = Cubic meter |
| ml | = Milliliter |
| mg | = Milligram |
| μm | = Micrometer |

| | |
|-------|--|
| MTZ | = Mass transfer zone |
| n | = Freundlich exponent (dimensionless) |
| nm | = Nanometer |
| PAC | = Powdered activated carbon |
| PDKAC | = Palm date kernel activated carbon |
| q_e | = Equilibrium solid-phase concentration (mg/g) |
| RAS | = Return activated sludge |
| SS | = Suspended solid |
| THMs | = Trihalomethanes |
| U.A.E | = United Arab Emirates |
| VOCs | = Volatile organic compounds |
| WWTP | = Wastewater treatment plant |

CHAPTER 1

INTRODUCTION & PROBLEM DEVELOPMENT

CHAPTER 1

INTRODUCTION & PROBLEM DEVELOPMENT

1.1 General

From the early 1970s to about 1980, wastewater treatment objectives were based primarily on aesthetic and environmental concerns. The earlier objectives of BOD, suspended solids, and pathogenic organisms reduction continued but at higher levels. Removal of nutrients such as nitrogen and phosphorus also began to be addressed, particularly in some of the inland streams and lakes. Effort was undertaken to achieve more effective and widespread treatment of wastewater to improve the quality of the surface water. This effort resulted in part from (1) an increased understanding of the environmental effects caused by wastewater discharges; (2) a developing knowledge of the adverse long-term effects caused by the discharge of some of the specific constituents found in wastewater; (3) the development of national concern for environmental protection. The result of these efforts was a significant improvement in the quality of the surface waters.

Since 1980, because of increased scientific knowledge and an expanded information base, wastewater treatment has begun to focus on the health concerns related to toxic and potentially toxic chemicals released to the environment. The water quality important

objectives of the 1970s have continued, but the emphasis has shifted to the definition and removal of toxic and trace compounds that may cause long-term health effects. As a consequence, while the early treatment objectives remain valid today, the required degree of treatment has increased significantly, and additional treatment objectives and goals have been added.

Sewage should be treated before its ultimate disposal into a receiving watercourse in order to: (a) reduce the spread of communicable diseases caused by the pathogenic organisms in the sewage; and (b) prevent the pollution of surface and ground water. These two reasons are interdependent to the extent that a polluted body of water is a potential and frequently an actual source of infection, particularly in hot climates.

Wastewater Treatment Techniques

The principle methods now used for the treatment of wastewater and sludge are identified in this section. Detailed descriptions of each method are not presented because the purpose here is only to introduce the many different ways in which treatment can be accomplished.

1. Preliminary and Primary Wastewater Treatment

Preliminary wastewater treatment is defined as the removal of wastewater constituents that may cause maintenance or operational problems with the treatment operations, processes, and ancillary systems. Examples of preliminary operations are screening and comminution for the removal of debris and rags, grit removal for the elimination of

coarse suspended matter that may cause wear or clogging of equipment, and floatation for the removal of large quantities of oil and grease.

In primary treatment, a portion of the suspended solids and organic matter is removed from the wastewater. This removal is usually accomplished with physical operation such as screening and sedimentation. The effluent from primary treatment will ordinarily contain considerable organic matter and will have a relatively high BOD. Treatment plants using only primary treatment will be phased out in the future as implementation of the EPA secondary treatment requirements is completed. Only in rare instances (for those communities having a secondary treatment waiver) will primary treatment be used as sole method of treatment. The principle function of primary treatment will continue to be as a precursor to secondary treatment.

Primary treatment will typically remove about 60 percent of the raw sewage suspended solids and 35 percent of the BOD₅.

2. Conventional Secondary wastewater Treatment

The major goal of secondary treatment is to remove the soluble BOD₅ that escapes the primary process and to provide added removal of suspended solids. Secondary treatment is typically achieved by using biological processes. These provide the same biological reactions that would occur in the receiving water if it had adequate capacity to assimilate the wastewater. The secondary treatment processes are designed to speed up these natural processes so that the breakdown of the degradable organic pollutants can be achieved in

relatively short time periods. Although secondary treatment may remove percent of the BOD₅ and suspended solids, it does not remove significant amounts of nitrogen, phosphorus, or heavy metals, nor does it completely remove pathogenic bacteria and viruses.

Secondary treatment is directed principally towards the removal of biodegradable organics and suspended solids. Disinfection is included frequently in the definition of conventional secondary treatment. Conventional secondary treatment is also defined as the combination of processes customarily used for the removal of these constituents and includes biological treatment by activated sludge, fixed-film reactors, or lagoon systems and sedimentation.

3. Nutrient Removal or Control

The removal or control of nutrients in wastewater treatment is important for several reasons. Nutrient removal or control is generally required for (1) discharges to confined bodies of water where eutrophication may be caused or accelerated, (2) discharges to flowing streams where nitrification can tax oxygen resources or where rooted aquatic plants can flourish, and (3) recharge of groundwater that may be used indirectly for public water supplies. The nutrients of principle concern are nitrogen and phosphorus that may be removed by biological, chemical, or a combination of the processes. In many cases, the nutrient removal processes are coupled with secondary treatment: for example, metal salts may be added to the aeration tank mixed liquor for the precipitation of

phosphorus in the final sedimentation tanks, or biological denitrification may follow an activated sludge process that produces a nitrified effluent.

4. Toxic waste Treatment/Specific Contaminant removal

The removal of toxic substances and specific contaminants is a complex subject. For industrial waste discharges to municipal collection and treatment system, pretreatment prior to discharge to the municipal system usually controls the concentrations of toxic pollutants. In some cases, removal of toxic substance is done at the municipal treatment facilities. Many toxic substances such as heavy metals are reduced by some form of chemical-physical treatment such as chemical coagulation, flocculation, sedimentation, and filtration. Some degree of removal is also accomplished by conventional secondary treatment. Wastewaters containing volatile organic constituents may be treated by air stripping or by carbon adsorption. Small concentrations of specific contaminants may be removed by ion exchange.

5. Advanced Wastewater Treatment

Although secondary treatment processes, when coupled with disinfection, may remove over 85 percent of the BOD and suspended solids and nearly all pathogens, only minor removal of some pollutants, such as nitrogen, phosphorus, soluble COD, and heavy metals, is achieved. In these cases, processes capable of removing pollutants not adequately removed by secondary treatment are used in what is called tertiary wastewater treatment (these processes have often been called advanced wastewater treatment).

- **Filtration**

By using a filtration process similar to that used in water treatment plants, it is possible to remove the residual suspended solids, including the unsettled bacteria. Removing the bacteria also reduces the residual BOD₅. Conventional sand filters identical to those used in water treatment can be used, but they often clog quickly, thus requiring frequent backwashing. To lengthen filter runs and reduce backwashing, it is desirable to have the larger particles of biological floc to be trapped at the surface without clogging the filter. Multimedia filters accomplish this by using low-density coal for the large grain sizes, medium-density sand for intermediate sizes, and high-density garnet for the smallest size filter grains. Thus, during backwashing, the greater density offsets the smaller diameter so that the coal remains on top, the sand remains in the middle, and the garnet remains on the bottom.

- **Carbon Adsorption**

Even after secondary treatment, coagulation, sedimentation, and filtration, the soluble organic materials that are resistant to biological breakdown will persist in the effluent. The persistent materials are often referred to as refractory organics. Refractory organics can be detected in effluent as soluble COD. Secondary effluent COD values are often 30 to 60 mg/l. The most practical available method for removing refractory organics is by adsorbing them on activated carbon.

In cases where secondary levels of treatment are not adequate, new treatment processes are applied to the secondary effluent to provide advanced wastewater treatment (AWT). Some of these processes may involve chemical treatment and filtration of the wastewater—much like adding typical treatment plant to the tail end of a secondary plant. Some of these processes can remove as much as 99 percent of BOD₅ and phosphorus, all suspended solids and bacteria, and 95 percent of the nitrogen.

1.2 Objectives and Impact of the Study.

Activated carbon is an adsorbent that is widely used in water treatment, advanced wastewater treatment, and in the treatment of certain organic industrial wastewater, because it adsorbs a wide variety of organic compounds. In water treatment, it is used to remove compounds, which cause objectionable taste, odor and color, and to adsorb toxic organic compounds.

The objective of the study is to produce activated carbon from readily available substances and study its physical and chemical characteristics and adsorption capacity.

The ultimate aim of this study is to investigate the use of locally available adsorbent material in place of commercial activated carbon, as an economic reliable alternative in polishing wastewater effluent.

The adsorbent used for this study is Palm Date Kernels Activated Carbon (PDKAC), which is easily available in the United Arab Emirates, and considered as non-biodegradable material. Phenol, aniline and methylene blue are selected as the trace contaminants used as adsorbate in the study.

The experimental study conducted to:

1. Determine treated wastewater effluent characteristics (residual chemical contaminants).
2. Examine the possibility of using and applying locally made adsorbents (i.e. Palm Date Kernels) to remove the trace organic contaminants.

The impact of this study is the upgrading of tertiary treatment (filtration) bed facilities in United Arab Emirates wastewater treatment plants using adsorbents prepared from locally available materials. This will lead to cost-effective method of effluent polishing, and will ultimately improve effluent quality for re-use in irrigation in the United Arab Emirates.

1.3 Tasks

Several tasks are required in carrying out the study. These include

- Carrying out a literature review to gather information on the chemical water contaminants and the available treatment technology.
- Preparation of activated carbon from locally available palm date kernels.
- Study the physical and chemical properties of the prepared activated carbon

- ❑ Devise an experiment to study the adsorption characteristics and adsorption capacity of the prepared PDKAC using standard procedures. Carry out adsorption tests using different adsorbates under laboratory conditions.
- ❑ Analyze the experimental data and discuss the results.

The tasks of this study have been done in three main laboratories, which are (a) Chemical Engineering Laboratories, U.A.E University, where the preparation and activation of Palm Date Kernels and determination of adsorption isotherms were done. (b) Zakher Wastewater Treatment Plant Laboratory, Al Ain Municipality, where the treated wastewater effluent characteristics (residual chemical contaminants) were determined, and (c) Central Laboratories Unit, U.A.E University, where the heavy metal analysis of wastewater effluent using Atomic Absorption and morphological characterization of adsorbent (PDKAC) by using Scanning Electron Microscope, were determined.

1.4 Thesis Organization

The thesis is organized in five (5) chapters as follows:

- 1) CHAPTER 1: Contains Introduction and Problem Development
- 2) CHAPTER 2: Contains Literature Review
- 3) CHAPTER 3: Contains Material and Methods
- 4) CHAPTER 4: Contains Results and Discussions
- 5) CHAPTER 5: Contains Summary and Conclusion
- 6) REFERENCES

CHAPTER 2

LITRATURE REVIEW

CHAPTER 2

LITERATURE REVIEW

2.1 PREPARATION OF ACTIVE CARBON

Activated carbon can be made from a variety of carbonaceous raw materials such as wood, coal and nutshells. Processing is dehydration and carbonization by slow heating in the absence of air followed by chemical activation to produce a highly porous structure. Powdered activated carbon (PAC) for water treatment, which has good characteristics for adsorption of taste and odor compounds, is commonly made from lignin or lignite. Granular activated carbon (GAC) made from coal has the best physical properties of density, particular size, abrasion resistance, and ash content. The characteristics are essential, since GAC is subject to filter backwashing, conveyance as slurry, and heat reactivation.

The activation process in manufacture creates a highly porous surface on the carbon particles with macropores and micropores down to molecular dimensions. Organic contaminants are adsorbed by attraction to and accumulation in pores of appropriate size, thus the pore structure is extremely important in determining adsorptive properties for particular compounds. In general, GAC most readily adsorbs branch-chained high-molecular-weight organic chemicals with low solubility. These include pesticides, volatile organic chemicals, and trihalomethanes. Micropores are large enough for colonies of bacteria to grow and proliferate if biodegradable organic compounds are in the water. The benefits of microbial growth or potential risks to

water quality are not well understood. GAC is reactivated thermally at a furnace temperature and retention time based on the volatility of the adsorbed chemicals. Two percent to 5% of the carbon is lost during each reactivation and must be replaced with fresh carbon.

2.1.1 Preparation Techniques

There is a wide variety of production and processing techniques used to manufacture of activated carbon, these are dependent on;

1. Nature and type of raw material available.
2. Desired physical form of the activated carbon.
3. Characteristics required for the intended application.

Active carbon can be prepared by chemical or physical activation method.

1. Chemical Activation

In the chemical activation method, the production of active carbon occurred by carbonization of the carbonaceous material with the addition of activating agents.

Chemical activation is used almost exclusively for carbons produced from materials of recent origin, usually wood waste (sawdust). The activating agent influences the pyrolytic processes so that formation of tar is restricted to a minimum and, the amount of the aqueous phase in the distillate (acetic acid, methanol, and others) is also less than in normal carbonization. The yield of carbon in the carbonized product is increased accordingly. Furthermore, the temperature needed for pyrolysis is also lower. Carbonization under their conditions yields a product, which, after removal of

the activating agent, has the properties of a good activated carbon. The most widely used activating agents are zinc chloride, potassium sulphide, potassium thiocyanate, phosphoric acid, sulphuric acid, sometimes hydroxides of the alkali metals, magnesium and calcium chloride and other substances are used.

The starting material is treated at an elevated temperature with the activating agent in the form of a concentrated solution, usually by mixing and kneading. The impregnated material is heated in a rotary kiln from which air is excluded (so called calcination) and pyrolytic decomposition takes place. The carbonized product from the kiln is cooled and the activating agent is then extracted from it.

2. Physical Activation

In the physical activation method, the active carbon is prepared by activating the carbonized intermediate products with gaseous agents. The carbonized intermediate product is prepared by carbonization of the carbonaceous material at higher temperatures.

The activating agents most often used are steam, carbon dioxide and oxygen (air); but chloride, sulphur vaporous, sulphur dioxide, ammonia and a number of other substances have activation effects, although they are rarely used for this purpose.

During the activation of the carbonized intermediate product first the disorganized carbon is removed, and by this the surface of the elementary crystallites become exposed to the action of the activating agent. The burning out of the crystallites must

proceed at different rates on different parts of the surface exposed to reaction; otherwise new pores could not be formed.

A possible explanation of the mechanism is that the velocity with which the crystallites burn is larger in the direction parallel with the plane of the carbon layers than in the direction perpendicular to this plane (Grisdale and Appl, 1953). The crystallites orientated perpendicularly to the surface exposed to the action of the activation agents can, therefore, be more easily attacked and burn out more quickly (Dannenbergh and Buonstra, 1955).

The removal of unorganized carbon and the non-uniform burnout of elementary crystallites lead in the first phase of activation, the formation of new pores-to the development of the macroporous structure. In the subsequent phases, however, the effect, which becomes increasingly significant is the widening of existing pores or the formation of larger size pore by the complete burnout of the walls between adjacent micropores. This leads to an increase in the volume of transitional and micropores, whereas the volume of micropores diminishes. As a measure of the degree of activation the so called burn-off which is the percentage weight decrease of the material during activation, referred to the weight of the original carbonized product. Sometime the so-called activation yield is used, which is the weight of the resulting active carbon expressed as a percentage of the carbonized intermediate product prior to activation. The burn-off (B) and the activation yield (A) are related thus

$$B=100-A$$

(2-1)

According to Dubinin and Zaverina (1949), when the burn-off is less than 50 percent, a microporous active carbon is obtained, when it is larger than 75 percent a macroporous product is obtained, and when the burn-off is between 50 and 75 percent the product is of the mixed structure and contains both micro-and macropores. The carbon atoms which form the structure of the carbonized intermediate product differ markedly from one another in their affinity towards the activation agent.

Those at the edges and corners of elementary crystallites, and those situated at defective places of the crystal lattice, are more reactive, because their valencies are incompletely saturated by interaction with neighboring carbon atoms. These places are the so-called active sites on which reaction with the activation agent occurs. Some authors assume that a carbon has different kinds of active sites, for which are reactive to carbon dioxide (Long and Sykes, 1948).

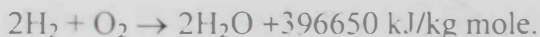
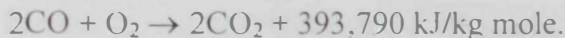
3. Steam Activation Mechanism

This technique is generally used for the activation of coal and coconut shell raw material, which is usually processed in a carbonized form. Activation is carried out at temperatures of 800-1100 °C in the presence of steam (www.activated-carbon.com).

Initially, gasification of the carbonised material with steam occurs, a reaction known as the Water-Gas reaction:



This reaction being endothermic, temperature is maintained by partial burning of the CO and H₂ formed:



The air is added so as to burn the gases without burning the carbon and the resultant activated carbon is graded, screened and de-dusted.

Activated carbons produced by steam activation generally exhibit a fine pore structure, ideal for the adsorption of compounds from both the liquid and vapor phase.

2.1.2 Types of Activated Carbon

1. Powdered active carbons (PAC)

Powdered active carbon in which particle diameter between 5 and 100 μm, is used for adsorption from solution. Disintegration into fine particle enhances the rate of establishment of adsorption equilibrium; this proceeds very slowly in liquids because of the low rate of diffusion.

Treatment with Powdered Activated Carbon

An alternative means of application is that of adding PAC. Powdered activated carbon has been added to the effluent from biological treatment processes, directly to the various biological treatment processes, and in physical-chemical treatment process-flow diagrams. In the case of biological-treatment-plant effluent, PAC is added to the effluent in a contacting basin. After a certain amount of time for contact, the carbon is

allowed to settle to the bottom of the tank, and the treated water is then removed from the tank. Because carbon is very fine, a coagulant such as a polyelectrolyte may be needed to aid the removal of the carbon particles, or filtration through granular-medium filters may be required. The addition of PAC directly in the aeration basin of an activated-sludge treatment process has proved to be effective in the removal of a number of soluble refractory organics.

Powdered activated carbon (PAC) is a fine powder applied in water slurry, which can be added at any location in the treatment process ahead of filtration. At the point of application, the mixing must be adequate to ensure dispersion and the contact time long enough for adsorption. The dosage for normal taste and odor control is usually up to 5mg/l with a contact time of 10-15 min.

2. Granulated active carbons (GAC)

Granulated active carbon in which particle diameter between 0.25 and 4 mm. The granular active carbon can be either crushed or pressed.

- Crushed active carbon is prepared by activation with a gaseous agent (steam, flue gases), a lump material, for example coke, carbonized shells, husks, etc. Crushed activated carbon can also be obtained by chemical activation.
- Pressed active carbon, which produced as uniform cylindrical shapes the starting material, a prepared plastic mass, is extruded from a die and the rod is cut into pieces of uniform length. By chemical or physical activation the active carbon was obtained.

Treatment with Granular Activated Carbon

A fixed-bed column is often used as a means of contacting wastewater with GAC. The water is applied to the top of the column and withdrawn at the bottom. The carbon is held in place with an under-drain system at the bottom of the column. Provision for backwashing and surface washing is usually necessary to limit the headloss buildup due to the removal of particulate material within the carbon column. Fixed-bed columns can be operated singly, in series, or in parallel.

Expanded-bed and moving-bed carbon contactors have also been developed to overcome the problems associated with head loss buildup. In the expanded-bed system, the influent is introduced at the bottom of the column and allowed to expand, much as a filter bed expands during backwash. In the moving-bed system, spent carbon is displaced continuously with fresh carbon. In such a system, head loss does not build up with time after the operating point has been reached.

Granular activated carbon (GAC) has been used for many years to solve water problems. Chlorine removal from water supply is efficiently handled by activated carbon filtration. Very little contact time is required to make this reaction occur. Color, taste and odour in water can be caused by organic material. The activated carbon adsorbs the organic matter and traps it in the porous surface of the granular particles. The adsorption of specific organic materials varies with the contact time.

Use of granular activated carbon (GAC) in wastewater system is a proven process for removal of organic compounds. As a tertiary treatment method, carbon adsorption and

regeneration have been used for a number of years to process domestic wastewaters with industrial wastes of organic origin as well as biologically treated wastewaters.

Design of a GAC system requires pilot-plant tests for selection of the best carbon, determination of the required contact time, the effects of influent water quality variations, and to establish the carbon loss during reactivation. The analytical methodology includes data on (1) adsorbability of the various organic compounds present, (2) performance of several different GACs in their removal, (3) information on the kind of process for reactivation, (4) frequency of reactivation, and (5) balancing costs of increased contact time against savings from less frequent reactivation.

2.1.3 Activated Carbon Production

There are a wide variety of production operations used in the manufacture of activated carbons, these are dependent on;

- Nature and type of raw material available.
- Desired physical form of the activated carbon.
- Characteristics required for the intended application.

Activated carbon is prepared by first making a char from materials such as almond, coconut, and walnut hulls, other woods, and coal. The char is produced by heating the material to a red heat in a retort to drive off the hydrocarbons but with an insufficient supply of air to sustain combustion. The char particle is then activated by exposure to an oxidizing gas at a high temperature. This gas develops a porous structure in the char and thus creates a large internal surface area. The surface properties that result is

a function of both the initial material used and the exact preparation procedure, so that many variations are possible. The type of base material from which the activated carbon is derived may also effect the pore-size distribution and the regeneration characteristics. After activation, the carbon can be separated into or prepared in different sizes with different adsorption capacities. The two size classifications are powdered, which has a diameter of less than 200 mesh, and granular, which has a diameter greater than 0.1 mm.

Data on the world production of active carbons are given in Table 2- 1. The output and the types of carbon manufactured depend strictly on the existing demand.

Table 2-1. World production of active carbon

| Region | Output, kilotons /year | | |
|----------------------|------------------------|----------|----------|
| | total | powdered | granular |
| North America | 127 | 75 | 52 |
| Japan | 40 | 25 | 15 |
| Asia & South America | 20 | NA | NA |
| Western Europe | 100 | 75 | 25 |

The Factors Influencing Design and Operation.

There is a wide number of variables, which influence the design, and operation of liquid phase absorption systems. This section has been prepared to highlight some of the factors, which should be considered, and to introduce the techniques that are available to define the effects of these variables. (Carbon Link, www.activated-carbon.com).

In general, the areas, which need to be identified, are;

Data on processing conditions:

- Concentration of adsorbate
- Temperature of the liquid stream
- pH of liquid stream
- Flow rates and operating frequency
- Pressure drop in system

Identification of characteristics of adsorbent:

- Relative molecular mass
- Solubility of adsorbate
- Concentration relative to solubility limits
- Polarity of adsorbate
- Temperature of solution

Selection of adsorbent for optimum efficiency

- Study of adsorption isotherm data
- Selection of optimum activity level
- Selection of optimum particle size
- Cost analysis
- Consideration of thermal reactivation.

2.2 ADSORPTION MECHANISMS

2.2.1 Activated Carbon Adsorption

In the past, the adsorption process has not been used extensively in wastewater treatment, but demands for a better quality of treated wastewater effluent have led to an intensive examination and use of the process of adsorption on activated carbon. Activated carbon treatment of wastewater is usually thought of as a polishing process for water that has already received normal biological treatment. The carbon in this case is used to remove a portion of the remaining dissolved organic matter. Depending on the means of contacting the carbon with the water, the particulate matter that is present may also be removed.

Adsorption, in general, is the process of collecting soluble substances that are in solution on a suitable interface. The interface can be between the liquid and gas, a solid, or another liquid. Although adsorption is used at the air-liquid interface in the floatation process, only the case of adsorption at the liquid-solid interface will be considered in this study (Metcalf and Eddy, 1991).

Adsorption is a unit operation by which a solute is concentrated at the surface of a solid. This phenomenon takes place when such a surface is placed in contact with a solution. A layer of molecules of solute accumulates on the surface of the solid due to imbalance of forces.

In the interior of the solid molecules are completely surrounded by similar molecules and therefore subjected to balanced forces. Molecules at the surface are subjected to nonbalanced forces. Because these residual forces are sufficiently strong, they may imprison molecules of the solute with which the solid is in contact. This phenomenon is called physical or Van der Waals adsorption. One distinction is that adsorption in case of water treatment uses an adsorbent solid processed especially for water treatment. The solid is termed the sorbent and the solute being sorbed is the sorbate.

Sorbent may either be finely powdered materials, applied to water in a clarifier or ahead of the filter, or 0.5 to 1.0mm granules contained in a vessel similar to a pressure filter. By far, the most common adsorbent used in water treatment is activated carbon, which may be used both in powdered and granular forms. Other adsorbents include a variety of clays, magnesium oxide, bone char, and activated alumina.

Major Uses of Liquid-phase Adsorption:

1. decolorizing, drying, or degumming of fuel and lubricants, organic solvents, vegetable oils, and animal oils
2. Recovery of biological chemicals (antibiotics, vitamins, flavoring) from fermentation broths or plant extracts

3. Clarification of food and drug products
4. Decolorizing of crude sugar syrups
5. Purification of process effluents for pollution control
6. Water-supply treatment for odor, taste, or color improvement
7. Separation of isomeric aromatic or aliphatic hydrocarbons.

(Perry and Green, 1984).

Adsorption is partially the result of forces of attraction at the surface of a particle that cause soluble organic materials to adhere to the particle, and partially attributable to the limited water solubility of many organic substances. Activated carbon has a large and highly active surface area that results from the activation process. This produces numerous pores within the carbon particle and creates active sites on the surface of the pores.

Since adsorption is a surface reaction, a measure of the effectiveness of an adsorbent is its surface area. For carbon the total surface area is usually 600 - 1000 m²/g. The surface is negatively charged. In spite of this, the negative charge of most colloids in water does not deter adsorption of high molecular weight materials, since the molecular structure itself becomes the controlling factor as molecular weight increases.

Activated carbon dechlorinates and removes organics by the process of adsorption (Metcalf and Eddy, 1991). The solute molecules are adsorbed onto the surface of the granular activated carbon particles because the force of attraction to the carbon

surface is greater than the forces, which keep them dissolved in solution. Therefore, compounds that are less soluble in water will adsorb onto the carbon surface due to the increase in hydrophobic bonding (Mohamed and Antia, 1998). In general, adsorption is better for high molecular weight compounds since they typically have a lower solubility.

With activated carbon, the reactions are occurring on the surface of the particles. To ensure the highest possible capacity, therefore, each individual carbon particle should have a very high surface area. During manufacture, the carbon particles undergo high temperature treatment process, which leaves a highly porous skeleton like structure to the particle, with many adsorption sites. It has been estimated that 1 cubic foot of granular activated carbon can have a surface of nearly 5 square miles.

Activated carbon when contacted with water containing organic material will remove these compounds selectively by a combination of adsorption of the less polar molecules, filtration of the larger particles, and partial deposition of colloidal material on the exterior surface of the activated carbon. The extent of removal of soluble organics by adsorption depends on the diffusion of the particle to the external surface of the carbon and diffusion within the porous adsorbent. For colloidal particles, internal diffusion is relatively unimportant because of the particle size. Organic substances that pass through the column consist of strongly hydrophilic organic molecules such as carbohydrates and other oxygenated compounds.

The great advantage of activated carbon as an adsorbent lies in the possibility of reactivation (up to 30 or more times) without appreciable loss of adsorptive power. Usually, heating spent carbon to about 1700 °F in a steam-air atmosphere (thermal reactivation) does reactivation. This operation can be performed in multiple hearth furnaces or rotary kilns. Adsorbed organics are burned off, and activated carbon is restored basically to its initial adsorption capacity.

2.2.2 Adsorption from Solution

In the case of nonelectrolytes, a logical division is made according to the presence of adsorbate in dilute solution. The adsorption of electrolytes is treated briefly, mainly in term of the exchange of components in an electrical double layer either at the surface of a nonporous particle or in an ion exchanger or zeolite.

Sorption from solution yields several kinds of information on active carbon. First, we obtain the adsorption efficiency of a unit amount of active carbon for the given substance at its concentration in the solution. This test, which is useful for a quick informative evaluation of active carbon for practical purposes.

Secondly, the surface area of the pore size of the active carbon can be obtained. The surface area is, in principle, determined in the same way as it is in adsorption from the gaseous phase: the amount adsorbed at the point corresponding to the formation of a statistical monolayer of adsorbate is expressed as the number of molecules and multiplied by the effective cross-sectional area of one molecule in the adsorbed state.

The amount adsorbed from solution, which corresponds to the coverage of the surface, by a monomolecular layer is determined from the adsorption isotherm, just as for the gaseous phase. For active carbon the isotherm is often of the Langmuir type so that the limiting amount adsorbed gives directly the amount of adsorbate needed for forming a monomolecular layer.

Often the value of the effective area occupied by the adsorbate molecule depends also on the solvent and on its adsorbability on the given surface, on the pH of the liquid phase and its composition and on the nature of the adsorbent surface. Thus measurements of adsorption from solution give, as a rule, only relative surface areas; these are suitable for comparing samples that differ little in conditions of preparation, chemical nature of the surface, etc. but generally they cannot be taken as absolute values of the surface area.

The porosity of active carbon can be estimated from measurements of adsorption from solution by the method of "molecular probes" (Dubinin, 1936 and King, 1934). If we choose a series of substances of different molecular size so that their relative adsorption from solution will in some degree depend on the size of the pores, we can estimate from the relative adsorption the fraction of pores with a radius less than that of a given molecule. In further developing the method, Bond and Maggs (1949), measured the heat of wetting of organic liquids on carbonaceous substances. By differentiating the curves representing the dependence of the heats on the molar volume of the liquids, they obtained a distribution of the surface area according to the radius of the pores. Morrison and Miller (1955), in a somewhat different approach,

proposed to calculate the distribution of the surface of micropores according to their radius from measurements of adsorption of a series of aliphatic acids from aqueous solutions. It may be concluded that porosity determination on the basis of adsorption from solution is simple but much less developed and reliable than those based on adsorption from the gaseous phase.

Adsorption from solution can also give certain information about the chemical nature of the surface of active carbon. Graham (1955), in his already cited work compared the adsorption of methylene blue and metanil yellow on more than forty different carbonaceous adsorbents. The molecular size of both dyes is approximately the same and therefore the smallest size of pores accessible to them is also particularly the same. The two substances differ however, in ionic character; whereas methylene blue forms in aqueous solutions a cation, metanil yellow forms an anion. The presence of acid oxides on the surface of active carbons therefore limits the extent of the adsorption of metanil yellow compared with that of methylene blue; and according to Graham, the dependence of the degree of this limitation on the amount of acid groups on the surface of the carbonaceous adsorbent is approximately linear.

1. Adsorption of Phenol

Phenol and substituted phenols are very common contaminants in water. Singer (1980); in fact, phenolic compounds constitute the 11th of the 126 chemicals, which have been designated as priority pollutants by the U.S. Environmental Protection Agency (Chapman *et al.* (1982)).

Numerous organic chemicals and inorganic chemical mostly heavy metals are classified as toxic pollutants. To qualify as a priority toxin, a substance must be an environmental hazard and known to be present in the water. Phenols are among the most important of the aromatic compounds. The mono hydroxy derivative of benzene is known as phenol. Phenols are industrial compounds used primarily in production of synthetic phenols, pigments and pesticides. Phenols are found to occur in domestic and industrial water, natural waters and potable water supplies. Phenol renders water toxic even at very low concentrations, its presence makes it very difficult or even impossible to prepare potable water from wastewater.

Phenols impart objectionable taste and odor at very low concentrations, taint fish and vary in toxicity depending on chlorination of the phenolic molecule. The U.S Public Health Service has fixed a limit of phenol, as 0.001 mg/l in drinking water. The removal of phenolic taste and odor from water supply is a serious challenge to engineers and water chemists.

Phenol is one of the most frequently occurring contaminants in wastewater.

Furthermore, an undesirable feature of phenol is that in the chlorination process, which is often a further purification step in water treatment, reaction with the chlorine produces carcinogenic chlorinated and polychlorinated compounds, e.g. trichlorophenols.

A number of processes have been proposed for the removal of phenol from wastewaters. In some, the phenols are only removed whereas in others, for instance, the koppers steaming process, extraction with organic solvents, and adsorption on activated carbon, they are recovered (Sierp, 1953).

One method is adsorption on activated carbon, which was first developed by the Carbo Norit in Germany (Sharp, 1961). The most modern apparatus for phenol removal with activated carbon is the fluidized-bed adsorber in which the carbon is fluidized by the treated water and is continuously exchanged (Kulski, 1959).

Adsorption on activated carbon is often used for purifying wastewaters from chemical plants making toxic substances, for example, insecticides, herbicides, pesticides and others (Sharp, 1961 and Giebler, 1958). Filters containing activated carbon are also used for filtering wastes from the manufacturing of detergent (Joyce, 1964).

Drozhalina *et al.* (1974) investigated the specific surface of active carbon. This study indicated that the specific surface area of activated carbon can be determined from the total amount of phenol adsorbed by carbon from 1% aqueous phenol solution. The calculations were made assuming that 2.64 m^2 of carbon is occupied by 1g of phenol. The determination gives results in a good agreement with those obtained by the more complex method that can be applied for activated carbon having low value of the structure constant B and the intermediate size pores ($0.25 - 0.34 \text{ cm}^3/\text{gm}$).

Leach *et al.* (1974) investigated a simplified analytical method to test for the adsorption power of activated carbon, by mechanical shaking 0.2 gram of carbon with 100 ml of 50 PPM of phenol solution in 250 ml flask, filtrate, and phenol solution were read at 270 nm.

Kitagawa and Hiroshi (1975) studied the adsorption of phenol, *p*-nitrophenol and 2,4-dichlorophenol in aqueous solutions by activated carbon. The adsorption characteristics of the above mentioned phenols from aqueous solutions were examined. The adsorption of these adsorbates was described by the Freundlich isotherms. The absorbed amounts at a given concentration decreased as the temperature increased, whereas the adsorption rate increased as the temperature increased. For the adsorption of phenol, the activation energy of diffusion is 6.3 kcal/mol.

Rate and equilibrium measurements of adsorption of two component adsorbates from dilute aqueous solutions by activated carbon were performed by Misic and Suzuki (1975) the measurements were carried out at 30 °C in a batch-operated stirred-tank reactor equipped with a basket mixer containing activated carbon. Concentration changes versus time were determined, for single adsorbate and for both the simultaneous and successive adsorption of phenol-propanoic acid and phenol-n-hexanoic acid systems, by use of ultraviolet and total organic carbon analysis. Isotherms of two component systems were expressed by a Freundlich equation for each component within a limited range of concentrations. These isotherms were compared with the isotherms obtained for single components over the same concentration range. Intraparticle diffusion is considered to be surface diffusion dominate, and the diffusivities determined from single component experiments could be used to explain the concentration changes in the multiple component systems.

Koganovski *et al.* (1976) studied the effect of energy of adsorption interaction on the rate of adsorption of organic substances from aqueous solutions by activated carbon. This study indicated that on increasing adsorption interaction energy, the adsorption rate increased, and since the adsorption was limited by the internal diffusion of molecules the rate of the diffusion of molecules the rate of the diffusion increased. Experimental data are given on the standard free energy- Δ^0F , and the adsorption rate as the time, $t_{1/2}$ of adsorption of 0.5 of the equilibrium adsorbed amount of phenol, 1-pentanol, 1-hexane, aniline, *p*-chloroaniline and β -naphthylamine from aqueous solutions on carbon KAD. The kinetic of adsorption were determined.

The kinetics of adsorption of phenols by granular activated carbon were investigated by Zogorski *et al.* (1976) this study showed that the removal of phenols from aqueous solutions via activated carbon adsorption is a feasible approach to diminishing the concentration of these contaminants in drinking waters. The kinetics of adsorption at equilibrium which are dependent on the physical and chemical characteristics of the adsorbate, adsorbent and experimental system were studied to determine the effect of parameters such as pH, initial adsorbate concentration, size of adsorbent, competitive adsorption, and type of adsorbate on phenol adsorption.

Puri (1976) studied the adsorption of phenol from aqueous solutions by carbons in relation to their specific surface area. The adsorption of phenol by carbon blacks and activated carbons at 35 °C from aqueous solutions of moderate concentration is largely reversible. The data when analyzed by a modified BET equation permit calculation of specific surface area of each adsorbent. Each isotherm shows a sharp

knee or plateau. This corresponds to completion of monolayer and therefore enables direct calculation of surface area. A small amount of phenol is also adsorbed irreversibly in some cases, but this can be separately accounted for, and therefore, does not interfere with the estimation of surface area.

The extent of adsorption of phenols at equilibrium is highly dependent upon the solubility of the adsorbate, the extent of proteolysis of the adsorbate, and the concentration of adsorbate equilibrated with the adsorbent. Zogorski and Faust (1978) found that the equilibrium of adsorption of phenols were independent of the mesh size of adsorption. Temperature has only a minor influence on the adsorption process, especially at high surface-coverage's. The adsorption of phenols appears to be a reversible process. The technical feasibility of removing phenolic compounds from aqueous solution via granular activated carbon adsorption is excellent.

Adsorption studies of phenol on granular and powdered activated carbon were carried out by Peel (1980) these studies showed that the granular activated carbon took < three weeks to reach equilibrium, but powdered activated carbon took from 3-5 days to reach equilibrium. Also the authors found that up to 80% of the adsorptive equilibrium was reached in the first few hours, but the remaining capacity was utilized very slowly. This type of behavior can be described by dual rate mechanism microprobe variations in isotherm behavior previously reported in the literature. Wherever possible, powdered carbon isotherms should be used instead of granular carbon isotherms.

Yakimova (1980) investigated a principle for selecting the structure of active carbons for removing organic substances from water. It is shown theoretically that the relation between concentration of an organic compound in wastewater and the degree of activated carbon pore filling (θ) by the organic compound is independent of the carbon type and only depends on the type of the organic compound. The foregoing was verified experimentally using common activated carbons of different porosity and aqueous of phenol, 2, 4 -dibromophenol and p-chloroaniline.

The mechanism of adsorption of trace amounts of phenol and anionic surfactant SDS by carbon adsorbents, e.g., activated carbon and conductive black under competitive conditions, in aqueous solution was studied by Asakawa (1986) adsorption isotherms for carbon adsorbents were all of the Freundlich-type. The total amount of linearly with increasing molar fraction of SDS at the initial concentration. Thus, the total amount adsorbed in the multi-solute system can be estimated by Freundlich constants determined from single-solute equilibrium adsorption and molar fractions of adsorbate at the initial concentration. The adsorbed amount of phenol for carbon black increased with the molar fraction of phenol at the initial concentration. The amount of adsorbed SDS for carbon black also increased with the molar fraction of phenol. These characteristics of SDS are closely related to the molecular size of SDS and to the pore structure of carbon black with meshpores.

Jing (1987) studied the competitive adsorption of various phenols in water onto granular active carbon. This study showed that the adsorption capacity is greater for o-nitrophenol, o-chlorophenol, o-cresol and o-methoxyphenol than phenol. The

adsorption of the individual compounds follows the Freundlich isotherms. At < 420 $\mu\text{mol/l}$ concentrations, the capacity for the compounds (except phenol) decreases with an increase in their numbers.

Mostafa *et al.* (1989) studied the adsorption of some phenols on steam-activated carbon. In this study the adsorption isotherms have been found to be first order in the low concentration range giving a plateau at high bulk solution concentrations. The thermodynamic parameters for the adsorption of o-chlorophenol and resorcinol have been calculated on the basis of Everett's isotherm equation.

Singer and Yen (1980) studied the adsorption of phenol and alkyl phenols on activated carbon for single- and multi-component systems. The adsorption behavior of single-component systems was found to confirm the Langmuir adsorption isotherm. For bisolute systems, the Langmuir competitive model did not adequately characterize the adsorption of alkyl phenols on activated carbon. The ideal Adsorption Solution (IAS) theory was successfully used to characterize competitive adsorption among alkyl phenols in two- and three-component systems.

Costa and Rodrigues (1982) studied the adsorption of phenol and p-nitrophenol in an aqueous solution on granular activated carbon. They have also reported the successful interpretation of their experimental data by IAS theory formulated by Radke and Prausnitz (1972); Moon and Tien (1987) have discussed further advancement of multi-component adsorption equilibria based on IAS theory.

2. Adsorption of Methylene Blue

Almost all industries use dyes and pigments to color their products, many of these dyes are inert and non-toxic at the concentrations discharged into the receiving waters. However, some are not so innocuous and in either case, the color they impart is very undesirable to the water user.

The methylene blue value gives an indication of the adsorption capacity of an active carbon for molecules having similar dimensions to methylene blue; it also gives an indication of the specific surface area of the carbon, which results from the existence of pores of dimensions greater than 1.5 nm.

The methylene blue value is defined as the number of cubic centimeters of standard methylene blue solution decolorized by 0.2 g of the active carbon (dry basis). The standard solution is prepared by dissolving 1.5 g of methylene blue (preferably of Merck medical, chemically pure, free from zinc chloride grade), so as to obtain 1 dm³ of solution. According to the DAB 7 method (Ishibashi, 1972) the standard methylene blue solution is added portion wise over 5 min with shaking to 200 mg of active carbon ground (< 0.1 mm) and dried at 150 °C. The methylene blue value is the number of cubic centimeters of the solution that been decolorized.

The decolorizing efficiency of the carbons obtained was investigated by determining the adsorption degree of methylene blue at different concentrations.

Studies on recycle system of dyeing wastewater were investigated by (Kuwabara and Shigeru 1985). In this study, the adsorption behavior of model dyeing wastewater

containing surfactants, dyes, and salts on activated carbon at < 80 °C and regeneration of the adsorbent by solvent were studied. The adsorption of acid and direct dyes and surfactant increased with increasing integral pore volumes of activated carbon. The saturation and adsorption decreased with increasing molecular weight of dyes and decreasing oxyethylene chain length in surfactants. The breakthrough capacity of activated carbon increased with increasing temperature of the wastewater. The anionic dye and surfactant adsorption increased with decreasing pH of the wastewater, due to reduced solubility of dyes, and this effect was enhanced with increasing number of sulfo groups in the dye and surfactants. Maximum desorption of spent adsorbent was obtained with mixed solvents having solubility parameter 14-18.

Barton and Stuart (1987). Studied the adsorption of methylene blue by activated carbon from aqueous solution. This study indicated that the adsorption of methylene blue is a convenient indicator in the evaluation of active carbons. The adsorption processes, is however, complicated by factors inherent in the structures of both methylene blue solution and the active carbon. These factors include the tendency of methylene blue to form molecular aggregates in solution, molecular sieving imposed by the pore size distribution of the carbon and the heterogeneous nature of the energies of adsorption and calorimetric experiments show, however, that the results obtained can be rationalized on the basis of these structural factors and kinetic effects which result from them.

Adsorption of methylene blue from aqueous solutions on the carbon prepared from rice husks was investigated by Youssef *et al.* (1990); the surface properties were

measured either by nitrogen adsorption at 77°K or carbon dioxide adsorption at 298 °K. From the sorption data the specific surface area of the prepared carbon has been calculated and the changes brought about by each activation process were discussed.

2.3 ANALYSIS OF THE ADSORPTION PROCESS

The adsorption process takes place in three: macrotransport, microtransport, and sorption. Macrotransport involves the movement of the organic material through the water to liquid-solid interface by advection and diffusion. Microtransport involves the diffusion of the organic material through the macropore system of the GAC to the adsorption sites in the micropores and submicropores of the GAC granule. Adsorption occurs on the surface of the granule and in the macropores and mesopores, but the surface area of these parts of the GAC granule are so small compared with the surface area of the micropores that the amount of material adsorbed there is usually considered negligible. Sorption is the term used to describe the attachment of the organic material to the GAC. When the rate of sorption equals the rate of desorption, equilibrium has been achieved and the capacity of the carbon has been reached. The theoretical adsorption capacity of the carbon for a particular contaminant can be determined by performing its adsorption isotherm.

The quantity of adsorbate that can be taken up by an adsorbent is a function of both the characteristics and concentration of adsorbate and the temperature. Generally, the amount of material adsorbed is determined as a function of the concentration at a constant temperature, and the resulting function is called an *adsorption isotherm*.

Equations that are often used to describe the experimental isotherm data were developed by Freundlich, by Langmuir, and by Brunauer, Emmet, and Teller (BET isotherm), (Show (1966); EPA (1973)). Of the three, the Freundlich isotherm is used most commonly to describe the adsorption characteristics of the activated carbon used in water and wastewater treatment.

2.3.1 Freundlich Isotherm

Freundlich liquid phase isotherm studies can be used to determine the adsorptive capacity of activated carbon over a range of different concentrations. Under standard conditions, the adsorptive capacity of activated carbon will increase as the concentration increases, until the maximum saturation capacity is achieved.

Freundlich liquid phase isotherm can be used to determine the effect of solubility on the adsorptive capacity of activated carbon over a range of different concentrations.

Phenol is highly soluble due to its polar nature whilst, in comparison, tetrachloroethylene has a low solubility due to being non-polar.

The empirically derived Freundlich isotherm is defined as follows.

$$q = x/m = a C_e^{1/n} \quad (2-1)$$

Where

x/m = amount of adsorbate adsorbed per unit weight of adsorbent (carbon)

C_e = equilibrium concentration of adsorbate in solution after adsorption

a, n = empirical constants.

The constants in the Freundlich isotherm can be determined by plotting (x/m) versus C_e and making use of Equation 2-1 rewritten as

$$\log (x/m) = \log a + 1/n \log C_e \quad (2-2)$$

2.3.2 Langmuir Isotherm

Derived from rational considerations, the Langmuir adsorption isotherm is defined as

$$q = x/m = a b C_e / (1 + b C_e) \quad (2-3)$$

Where

x/m = amount adsorbed per unit weight of adsorbent (activated carbon)

a, b = empirical constants

C_e = equilibrium concentration of adsorbate in solution after adsorption

The constants in the Langmuir isotherm can be determined by plotting $C_e/(x/m)$ versus C_e and making use of Equation 2-3 rewritten as

$$C_e/(x/m) = 1/a b + (1/a) C_e \quad (2-4)$$

2.3.3 Mass-Transfer Zone:

The area of the GAC bed in which sorption occurs is called the *mass transfer zone* (MTZ). After the contaminated water passes through a region of the bed whose depth is equal to the MTZ, the concentration of the contaminant in the water have been reduced to its minimum value. No further adsorption will occur within the bed below the MTZ. As the top layers of carbon granules become saturated with organic material, the MTZ will move down in the bed until breakthrough occurs. A certain minimum empty bed contact time is required for the MTZ to be developed fully within the GAC bed. If the empty bed contact time of the column is too short (i.e., the

hydraulic loading rate is too great), the length of the MTZ will be larger than the GAC bed depth, and the absorbable contaminant will not be completely removed by the carbon (Metcalf and Eddy, 1991).

The thickness of the MTZ varies with the flowrate because dispersion, diffusion, and channeling in a granular medium are directly related to the flowrate. The only way to use the capacity at the bottom of the column is to have two columns in series and switch them, as they are exhausted, or to use multiple columns in parallel. The optimum flowrate and bed depth, as well as the operating capacity of the carbon must be established to determine the dimensions and the number of columns necessary for continuous treatment.

The effect of linear flow rate through an activated carbon adsorption unit can be illustrated by the mass transfer zone (MTZ). Following a period in operation, the top portion of the bed will become fully loaded with adsorbed organics; this is referred to as the saturation zone. Removal of the dissolved organics takes place in the section of the bed referred to as the MTZ. The length of the MTZ can be optimized at lower linear flow rates. Other factors, such as concentration and particle size, will also affect the MTZ.

Initially, on start up of an adsorption unit, there will be a slight increase in the pH of the effluent water. This is due to trace leaching of the soluble matter from the matrix of the activated carbon. Leaching is usually controlled by efficient backwashing, which will readily remove soluble matter, following which the system will reach

equilibrium with the pH of the feed water.

Adsorption efficiency can be optimized by using finer particle size products, which improve the rate of diffusion to the surface of the activated carbon. This must be balanced against pressure drop limitations.

Efficient backwashing is an important part of the start up of an activated carbon filter. A bed expansion of 25-35% should be used to remove readily soluble matter and to stratify the particles, to ensure that the MTZ is maintained when future backwashing is undertaken.

2.3.4 Carbon Adsorption Capacity

The adsorptive capacity of the carbon can be estimated by extending a vertical line from the point on the horizontal scale corresponding to the initial concentration C_0 and extrapolating the isotherm to intersect this line. The $(x/m) C_0$ value at the point of intersection can be read from the vertical scale. This $(x/m) C_0$ value represents the amount of constituent adsorbed per unit weight of carbon when the carbon is at equilibrium with the initial concentration of constituent. This condition should exist in the upper section of a carbon bed during column treatment, and it therefore represents the ultimate capacity of the carbon for a particular waste.

2.3.5 Breakthrough Adsorption Capacity

In the field, the breakthrough adsorption capacity, $(x/m)_b$, of the GAC in a full-scale column is some percentage of the theoretical adsorption capacity found from the

isotherm. The $(x/m)_b$ of a single column can be assumed to be approximately 25 to 50 percent of the theoretical capacity $(x/m)_o$ (Schroeder and Techobanoglous, 1990). Once $(x/m)_b$ is known, the time to breakthrough can be calculated by solving the following equation (Schroeder and Techobanoglous, 1990).

$$(x/m)_b = X_b/M_c = Q (C_i - C_b/2) t_b/M_c \quad [8.34 \text{ lb/M gal. (mg/L)}] \quad (2-5)$$

Where:

- $(x/m)_b$ = field breakthrough adsorption capacity, lb/lb or g/g
- X_b = mass of organic material adsorbed in the GAC column at breakthrough, lb or g
- M_c = mass of carbon in the column, lb or g
- Q = flow rate, Mgal/d
- C_i = influent organic concentration, mg/L
- C_b = breakthrough organic concentration, mg/L
- t_b = time to breakthrough, d

Equation (2-5) was developed assuming that C_i is constant and that the effluent concentration increases linearly with time 0 to C_b . Rearranging Equation (2-5), the time to breakthrough can be calculated using the following relationship.

$$t_b = (x/m)_b M_c / Q [C_i - (C_b/2)] \quad [8.34 \text{ lb/M gal. (mg/L)}] \quad (2-6)$$

For a powdered-carbon application, the isotherm adsorption data is used in conjunction with a material-balance analysis to obtain an estimate of the amount of carbon that must be added (EPA, 1973). Here again, because of the many unknown

factors involved, pilot plant tests to develop the optimum design data are recommended.

2.4 WASTEWATER TREATMENT

2.4.1 Wastewater Composition (Pollutants)

Composition refers to the actual amounts of physical, chemical and biological constituents present in wastewater. In this section, data on the constituents found in wastewater seepage are presented. Discussions are also included on the need to characterize wastewater more fully and on the mineral pickup resulting from water use.

1. Constituents in Wastewater and Septage

Typical data on the individual constituents found in domestic wastewater are reported in Table 2-2. Depending on the concentrations of these constituents, wastewater is classified as strong, medium or weak. Both the constituents and the concentrations vary with the hour of the day, the day of the week, the month of the year. Therefore, the data in Table 2-2. are intended to serve only as a guide and not as a basis for design. Septage is the sludge produced in individual onsite wastewater-disposal system, principally septic tanks and cesspool. The actual quantities and constituents of septage vary widely. The greatest variations are found in communities that do not regulate the collection and disposal of septage.

Table 2-2. Typical composition of untreated domestic wastewater

| Parameter, mg/l | Concentration | | |
|---------------------------------|---------------|---------------|-------------|
| | <i>Strong</i> | <i>Medium</i> | <i>Weak</i> |
| Total solids | 1200 | 720 | 390 |
| Total dissolved solids | 850 | 500 | 250 |
| Volatile solids | 325 | 200 | 105 |
| Suspended Solids | 350 | 220 | 100 |
| Biochemical oxygen demand,5 day | 400 | 220 | 110 |
| Total Organic Carbon | 290 | 160 | 80 |
| Chemical oxygen demand | 1000 | 500 | 250 |
| Total Nitrogen | 85 | 40 | 20 |
| Organic Nitrogen | 35 | 15 | 8 |
| Free Ammonia | 50 | 25 | 12 |
| Phosphorus | 15 | 8 | 4 |
| Chlorides | 100 | 50 | 30 |
| Alkalinity as CaCO ₃ | 200 | 100 | 50 |
| Grease | 150 | 100 | 50 |

Metcalf and Eddy, (1991).

2. Microorganism in Wastewater

Representative data on the type and number of microorganisms commonly found in wastewater are reported in Table 2-3. The relatively wide variation in the reported range of values is characteristic of wastewater analysis. It has been estimated that up to 3 or 4 % of the total coliform group are pathogenic. Some organisms (shigella, helminth eggs, and protozoa cysts) are almost never looked for in a routine analysis. Great care should be exercised when reviewing reported virus values.

Table 2-3 Types and numbers of microorganisms typically found in untreated domestic wastewater

| Organism | Concentration, number/ml |
|--------------------------------|---------------------------------|
| Total coliform | 10^5 - 10^8 |
| Fecal coliform | 10^4 - 10^5 |
| Fecal streptococci | 10^3 - 10^4 |
| Enterococci | 10^2 - 10^3 |
| Salmonella | 10^0 - 10^2 |
| <i>Pseudomonas aeruginosa</i> | 10^1 - 10^2 |
| <i>Clostridium perfringens</i> | 10^1 - 10^3 |
| Protozoan cysts | 10^1 - 10^3 |
| Giardia cysts | 10^{-1} - 10^2 |
| Cryptosporidium cysts | 10^{-1} - 10^1 |
| Helminth ova | 10^{-2} - 10^1 |
| Enteric virus | 10^1 - 10^2 |

Metcalf and Eddy, (1991).

3. Need for Specialized Analyses

In general the constituents reported in Table (2-2). are those that are analyzed more or less routinely. In the past, it was believed that these constituents were sufficient to characterize a wastewater for biological treatment, but as our understanding of the chemistry and microbiology of wastewater treatment and environmental quality has continued to expand, the importance of analyzing additional constituents is becoming more appreciated.

These additional constituents that are now analyzed include many of the metals necessary for the growth of microorganisms such as calcium, cobalt, copper, iron, magnesium, manganese, and zinc. The presence or absence of hydrogen sulfide should be determined to assess whether corrosive conditions may develop and whether any trace metals necessary for the growth of microorganisms are being precipitated. The concentration of sulfate should be determined to assess the suitability of anaerobic waste treatment. The presence of filamentous organisms in the wastewater should also be determined, especially if biological treatment is being considered. Priority pollutants must be analyzed to determine if special treatment and control methods will be required to minimize the release of these compounds to the environment.

2.4.2 Characteristics of Domestic Wastewater

1. Physical Characteristics

Fresh, aerobic, domestic wastewater has been said to have the odor of kerosene or freshly tilled earth. Aged, septic sewage is considerably more offensive to the olfactory nerves. The characteristic rotten egg odor of hydrogen sulfide and the mercaptans is indicative of septic sewage. Fresh sewage is typically gray in color, while septic sewage is black.

Wastewater temperatures normally range between 10 and 20 °C. In general, the temperature of the wastewater will be higher than that of water supply. This is because of the addition of warm water from households and heating within the plumbing system of the structure.

One cubic meter of wastewater weighs approximately 1,000,000 grams. It will contain about 500 grams of solids. One-half of the solids will be dissolved solids such as calcium, sodium, and soluble organic compounds. The remaining 250 grams will be insoluble. The insoluble fraction consists of about 125 grams of material that will settle out of the liquid fraction in 30 minutes under quiescent conditions. The remaining 125 grams will remain in suspension for a very long time. The result is that wastewater is highly turbid.

2. Chemical Characteristics

Because the number of chemical compounds found in wastewater is almost limitless, we normally restrict our consideration to a few general classes of compounds. These classes often are better known by the name used to measure them than by what is included in the class. The COD test is used to determine the oxygen equivalent of the organic matter that can be oxidized by a strong chemical oxidizing agent (potassium dichromate) in an acid medium. The COD of a waste, in general, will be greater than the BOD_5 because more compounds can be oxidized chemically than can be oxidized biologically, and because BOD_5 does not equal ultimate BOD.

The COD test can be conducted in about three hours. If it can be correlated with BOD_5 , it can be used to aid in the operation and control of the wastewater treatment plant (WWTP).

The pH for all of these wastes will be in the range of 6.5 to 8.5, with a majority being slightly on the alkaline side of 7.

2.4.3 Classification of Wastewater Treatment Methods

The contaminants in wastewater removed by physical, chemical and biological means. The individual methods usually are classified as physical unit operations, and processes occur in a variety of combinations in treatment systems. It has been found advantageous to study their scientific basis separately because the principles involved do not change.

1. Physical Unit Operations

Treatment methods in which the application of physical forces predominates are known as physical unit operations. Because most of these methods evolved directly from man's first observations of nature, they were the first to be used for wastewater treatment. Screening, mixing, flocculation, sedimentation, flotation, filtration, and gas transfer are typical unit operations.

2. Chemical Unit processes

Treatment methods in which the removal or conversion of contaminants is brought about by the addition of chemicals or by other chemical reactions are known as chemical unit processes. Precipitation, adsorption, and disinfection are the most common examples used in wastewater treatment. In chemical precipitation, treatment is accomplished by producing a chemical precipitate that will settle. In most cases, the settled precipitate will contain both the constituents that were swept out of the

wastewater as the precipitate settled. Adsorption involves the removal of specific compounds from the wastewater on solid surface using the forces of attraction between bodies.

3. Biological Unit Processes

Treatment methods in which the removal of contaminants is brought by biological activity are known as biological unit processes. Biological treatment is used primarily to remove the biodegradable organic substances (colloidal or dissolved) in wastewater. Basically, these substances are converted into gases that can escape to the atmosphere and into biological cell tissue that can be removed by settling. Biological treatment is environmental control: wastewater can be treated biologically in most cases. Therefore, the engineer should provide the proper environment so that the process can operate effectively.

2.4.4 Wastewater Treatment Plant In Al Ain

Zakher wastewater treatment plant was designed for construction in two phases. Phase I has been designed to treat a flow of 27,000 m³/day dry weather flow (DWF), and was commissioned in 1981. Construction of phase II of the treatment plant started in 1989 and was completed in 1993, doubling the capacity of the works to treat a flow of 54,000 m³/day (DWF).

The wastewater-processing scheme at Zakher wastewater treatment plant is extended aeration for biological treatment followed by settlement tanks, and polishing of

effluent by dual-media rapid gravity sand filters and disinfection of effluent by chlorination.

The Zakher Wastewater Treatment Plant incorporates the following stages:

1. Screening

To remove large solids and rags, which are not biodegradable, such solids if passed through the plant may cause physical problems later in the treatment process.

2. Grit Removal

To remove 95% of grit and stones which could result in blockages and abrasive wear on machinery and pipe works.

3. Aeration Tanks

The incoming sewage, having been "seeded" with active organisms is passed through tanks equipped with surface aerators designed to provide atmospheric oxygen for the process and to ensure adequate mixing so as to maintain the sewage particles and organisms in suspension.

4. Settling Tanks

After the aeration process the activated sludge is allowed to settle, leaving an effluent containing less than 30 PPM of suspended solids.

5. Return Activated Sludge (RAS)

Some of this sludge from the settling tanks is returned to be mixed with incoming sewage to the aeration tanks, in order to seed active organisms into the process.

6. Effluent Filtration

Sand-bed filters remove a large percentage of the remaining suspended solids from the settlement effluent. Air scouring and backwash of the filters is used, when necessary, for cleaning, the backwash water being returned to the inlet of the works and mixed with incoming sewage.

7. Chlorination

Chlorine gas is injected into the final effluent for the purpose of disinfection before the effluent is pumped to the distribution network around Al Ain; residual chlorine content of 1 PPM is the desired final concentration.

8. Aerobic Digestion

Surplus activated sludge from the settling is further aerated to improve the stabilization and consolidation. At intervals, the digesting sludge is allowed to settle. top water is decanted and returned to the works inlet and the consolidated digested sludge is pumped to the drying beds.

9. Sludge Dewatering

Natural air-drying is used to obtain a dry sludge cake, which can be used as a soil-conditioning agent for agriculture, or horticulture proposes.

The classification and general specification of Zakher Wastewater Treatment Plant are shown in Table 2-4.

Table 2-4. The classification and general specification of wastewater treatment process at Zakher Wastewater Treatment Plant.

| UNIT | TYPE |
|--|---|
| <i>1. Sewage Treatment Units:</i> | |
| Screens | Hydraulic rake |
| Detroiters | Bladed grit collection scraper |
| Aeration Tanks | Rectangular tanks with surface aerators |
| Settlement Tanks | Circular with radial flow |
| Sand Filters | Three beds(garnet, sand, coal) filter |
| Chlorination | Chlorine vacuum feeders |
| <i>2. Sludge Treatment Units:</i> | |
| Aerobic Digesters | Circular with continuous rotation |
| Drying Beds | Square low depth beds |

CHAPTER 3

MATERIAL & METHODS

CHAPTER 3

MATERIAL & METHODS

3.1 MATERIAL

The materials required for this study include the prepared PDKAC, adsorbates and other equipment to carry out the necessary experiments. For example, according to the adsorption system, the materials required are the liquid phase and solid phase of the system, which act as adsorbate and adsorbent, respectively.

3.1.1 Adsorbent

Adsorbent is any solid material having the ability to concentrate significant quantities of other substances on its surface, or on its pore structure.

The solid material used as adsorbent is Palm Date Kernel Activated Carbon (PDKAC).

3.1.2 Adsorbate

Adsorbate is any substance that can be adsorbed, including organic compounds, color bodies and taste and odor by adsorbent.

The adsorbates used in this study are phenol, aniline and methylene blue.

3.2 EQUIPMENT

The adsorbent (PDKAC) was prepared in *bomb reactor calorimeter* and for particle size analysis, the *sieve shaker* (No. 1 BS 410 sieve of 75 μm aperture) was used. The adsorbent was analyzed for its carbon, hydrogen and nitrogen content using a *CHN Analyzer* model CE 440 (Lee Man USA). A *Fourier-transform infrared Shimadzu FTIR-8101 spectrophotometer* of 8.0 cm^{-1} resolution and 40 accumulation, fitted with a 2.8 mm/s detector and *Happ-Genzael apodization*, was used to determine and study the kinds of functional groups present on the surface of PDKAC.

The *scanning electron microscope* was used for morphological characterization.

3.3 METHODS

3.3.1 Preparation of Activated Carbon (Adsorbent)

The palm fruit kernels used in this study were collected from Al-Ain city, United Arab Emirates. Dry date kernels were subjected to a pyrolysis process at 750°C in the absence of air for 8 hrs. The resulting palm date kernel carbonizate was ground to the minimum possible size and sieved to pass through a No. 1 BS 410 sieve of 75 μm aperture. The palm date kernel carbonizate particles were then subjected to a steam activation process at 750°C for 8 hrs (Jankawska *et al.* 1991). Prior to their use in adsorption studies, the palm date kernel activated carbon (PDKAC) particles were washed several times using deionized water to remove any soluble impurities and subsequently dried in the absence of air at a temperature of 200°C for 24 hrs. They

were then stored in a desiccator prior to weighing for adsorption studies. infrared spectroscopic and surface area analysis.

3.3.2 Determination of Equilibrium Time

In order to determine the equilibrium time for maximum adsorption, the following experiment was carried out using phenol solution for different time intervals as described below.

A stock solution of phenol, 1.6g/l (1600ppm) was prepared. From this stock solution a working solution of 100-ppm phenol solution was prepared. 50ml of the prepared 100-ppm solution was transferred to seven different bottles. One g of the prepared PDKAC was added to each of the seven bottles. These bottles were then shaken on a stirrer placed over a water bath maintained at 25⁰C for different time intervals. After each time interval the specified bottles were removed.

The carbon content was then filtered using glass fiber filter papers. The filtrate was then analyzed for the remaining phenol content using the Pye Unicam PU8630 spectrophotometer at 270 nm wavelength and 0.2 ppm detection limit. The absorption values were then plotted against the time and the equilibrium time is calculated from the graph.

3.3.3 Adsorption Isotherms

Carbon samples (1g) were taken in flasks of 100-ml capacity, and 50 ml of the substrate solution Phenol of different concentrations (200-1600 ppm) were used. The flasks were continuously shaken in a water bath shaker kept at 25 °C until adsorption equilibrium was established. Equilibrium reached in all cases after the solutions were allowed to stand for 24 hrs.

The difference between the initial concentration (C_0) and the equilibrium concentration (C_e) was used to compute the amount of phenol removed (q_e) from the solution as follows:

$$q_e = 50(C_0 - C_e)/M \quad (3-1)$$

Where M is the mass of adsorbent employed (in g). All batch tests were carried out at ± 25 °C to eliminate any temperature effects.

The same experiments were repeated using Aniline and Methylene Blue as the substrate at a concentration of (200-1000 ppm) and (400-1800 ppm), respectively.

Blank samples for phenol, aniline, and methylene blue were prepared and no change in concentrations was found.

CHAPTER 4

RESULTS & DISCUSSIONS

RESULTS & DISCUSSION

4.1 Physiochemical Properties of PDKAC Adsorbent

The physiochemical properties of PDKAC adsorbent are shown in Table 4-1. In addition, CHN analysis confirmed the presence of a high percentage of carbon (75%) in addition to the existence of hydrogen and nitrogen. The lower bulk density of the PDKAC adsorbent (Lastoskie *et al.* 1990) as well as the aforementioned surface functional groups (Gergova *et al.* 1993, Cookson 1978) explain the ability of PDKAC to act as an adsorbent in the removal of trace contaminants from wastewater effluent.

Table 4.1 Physiochemical properties of locally-made PDKAC adsorbent

| | |
|-----------------------------------|--|
| Bulk density (kg/m ³) | 517 |
| Particle size (µm) | ≤75 |
| Carbon (wt. %) | 75.16 |
| Hydrogen (wt. %) | 2.68 |
| Nitrogen (wt. %) | 3.54 |
| Reminder (wt. %) | 18.62 |
| Ash content (wt. %) | 3.789 |
| Surface functional groups | : >N-H, >N ⁺ -H, -OH, -CH, -COOH, >C=O and -N=O |

4-2 Morphological Characterization of PDKAC Adsorbent.

The Scanning Electron Microscope pictures of the adsorbent, (PDKAC), which was used for the experiment are shown in Figures 4-1, 4-2, and 4-3. Figure 4-1 shows the arrangements of PDKAC units at a magnification of 35 times, while, Figure 4-2 identifies the pores inside one of the units shown in Figure 4-1 at a magnification of 550 times. Furthermore, at a higher magnification of 10,000 times, one will be able to identify the particles sizes at higher levels as well as the micropores.



Figure 4-1 Scanning electron microscope picture of PDKAC units (peds) and the macropores.



Figure 4-2 Scanning electron microscope picture of PDKAC unit showing pore sizes and their arrangements.

4.3 Interfacial Analysis

From the scanning electron microscope image in Figure 4-3, it can be seen that the particles are irregular in shape and size, and the surface is rough. The particles are distributed in a porous structure, and there are many micropores between the particles.

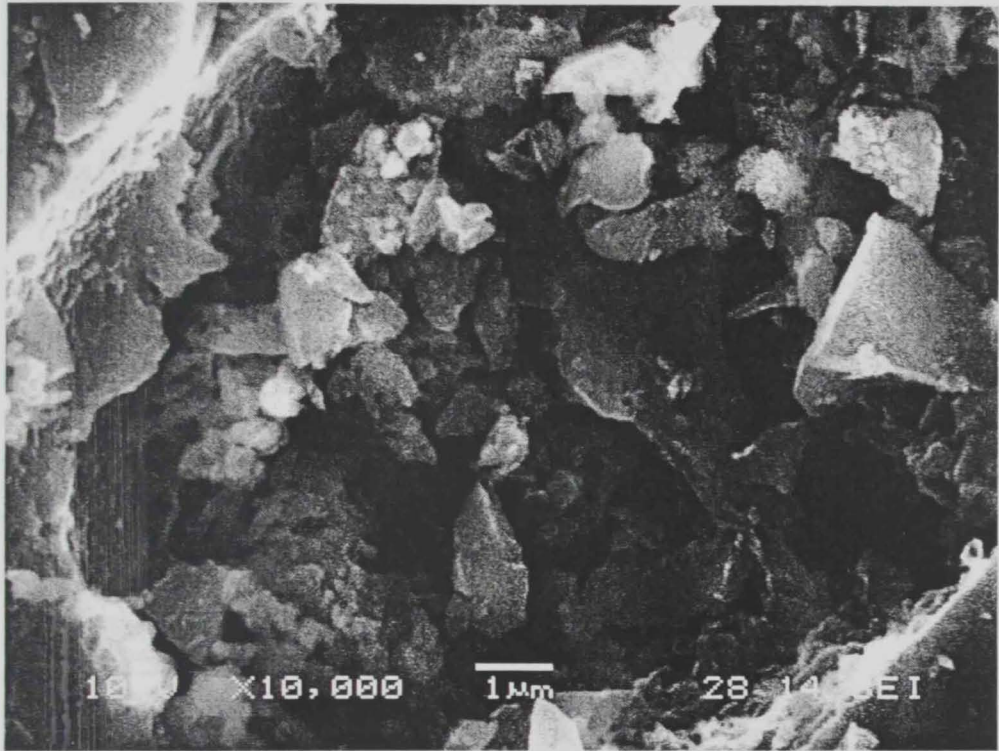


Figure 4-3 Scanning electron microscope picture of PDKAC particles and micropores.

4-3 Infrared Analysis.

From the infrared (IR) spectrum which is shown in Figure 4-4, PDKAC adsorbent contains the following surface functional groups: $>\text{N-H}$, $>\text{N}^+\text{-H}$, $-\text{OH}$, $-\text{CH}$, $-\text{COOH}$, $>\text{C=O}$ and $-\text{N=O}$ (Radwan and Nassar, 1997).

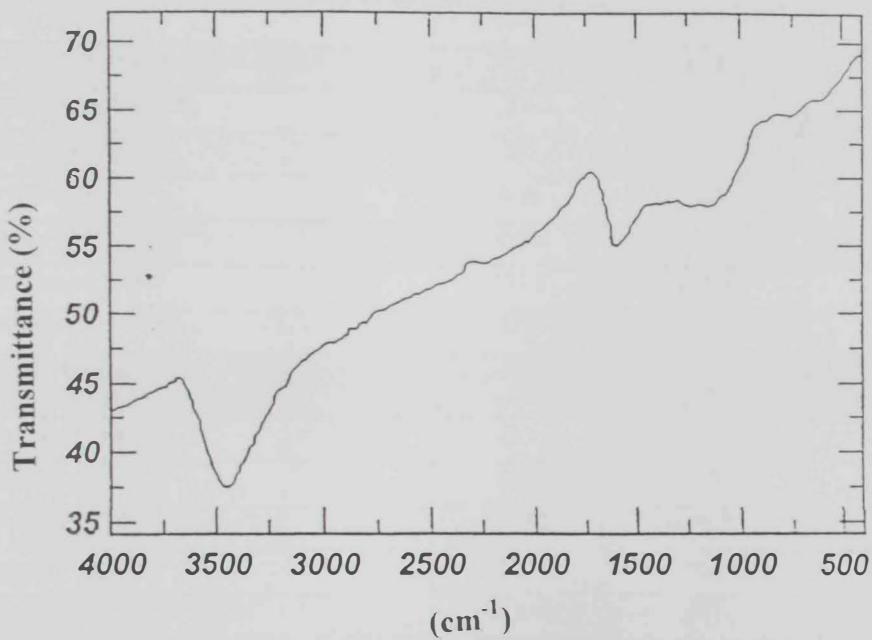


Figure 4-4 Infrared spectrum of PDKAC.

4-4 Typical Analysis of Zakher Wastewater Treatment Plant

The analysis results of the treated effluent from Zakher wastewater treatment plant (listed in Table 4-2) reflect the effluent characteristics and the treatment efficiency.

Table 4-2 Characteristics of final effluent at Zakher Wastewater Treatment Plant.

| Parameters | Settlement Overflow | Sand Filter (Chlorinated) | Intl. Potable Water Guidelines |
|---|---------------------|---------------------------|--------------------------------|
| pH | 7.4 | 7.4 | 6.5 – 8.5 |
| Total Dissolved Solids (TDS) | 1005 | 1011 | 500 |
| Ammonia as N | 1.64 | 0.10 | N/A |
| BOD ₅ | 2.05 | 0.6 | N/A |
| Chemical Oxygen Demand (COD) | 19.7 | 18.4 | N/A |
| Suspended Solids (SS) | 7.6 | 3.7 | N/A |
| Chloride as Cl | 267 | 275 | 250 |
| Nitrites as N | 0.16 | 0.04 | 1 |
| Nitrates as N | 1.92 | 1.2 | 10 |
| Sulphates as SO ₄ ⁻ | 157.8 | 157.8 | 250 |
| Total Hardness (TH) | 315 | 265 | N/A |
| Heavy Metals | | | |
| Cadmium (Cd) | ND | ND | 0.005 |
| Cobalt (Co) | ND | ND | N/A |
| Chromium (Cr) | 0.0902 | 0.0075 | 0.05 |
| Copper (Cu) | ND | ND | 1.3 |
| Iron (Fe) | 0.1135 | 0.0415 | 0.3 |
| Manganese (Mn) | 0.0400 | 0.0435 | 0.05 |
| Nickel (Ni) | ND | ND | 0.02 |
| Lead (Pb) | ND | ND | 0.01 |
| Zinc (Zn) | ND | ND | 3 |

All units are in mg/l except pH

ND = Non detected

4-5 Physiochemical Properties of Adsorbate Solutions

The physiochemical properties of Phenol, aniline and Methylene Blue are illustrated in Table 4-3

Table 4-3. The physiochemical properties of phenol, aniline and methylene blue

| | PHENOL | ANILINE | METHYLENE BLUE |
|----------------------------|--|--|---|
| Chemical Formula | C ₆ H ₆ O | C ₆ H ₅ N ₂ | C ₁₆ H ₁₈ N ₃ S Cl |
| Physical Properties | White Crystalline mass, soluble in alcohol, water and ether, flammable | Colorless oily liquid soluble in alcohol, ether | Dark green crystals soluble in water, alcohol, chloroform |
| Specific Gravity | 1.07 | 1.0235 | |
| Water Solubility | Slightly sol. 8.28 g/100mL | Moderately sol 3.5 g/100mL at 20 °C | |
| Molecular Weight | 94.113 | 93.128 | 319.85 |
| Melting Point | 40.5 °C | 6.2 °C | 190 °C |
| Boiling Point | 182 °C | 184.4 °C | |
| Flash Point | 78 °C | 70 °C | |
| Hazard | Toxic by ingestion, inhalation and skin absorption. Tolerance limit 5 ppm in air | Toxic by ingestion, inhalation, skin absorption. Tolerance limit, 2 ppm in air | Moderately toxic by ingestion |
| Uses | Production of epoxy resins and phenolic resins, which are used in the plywood, construction, automotive, and appliance industries. | Photography, explosives, herbicide, fungicide, petroleum refining | Dyeing cotton, bacteriological-stain indicator |

4.6 Equilibrium Time

The equilibrium time for the tested phenol as discussed previously in chapter 3 is shown in Figure 4-5.

From Figure 4-5 its evident that the amount adsorbed increases with time at constant temperature of 25°C , and also the adsorption rate reached the equilibrium point after 24 hrs. So, 24 hrs time has been selected as the equilibrium time for carrying out all subsequent batch adsorption tests.

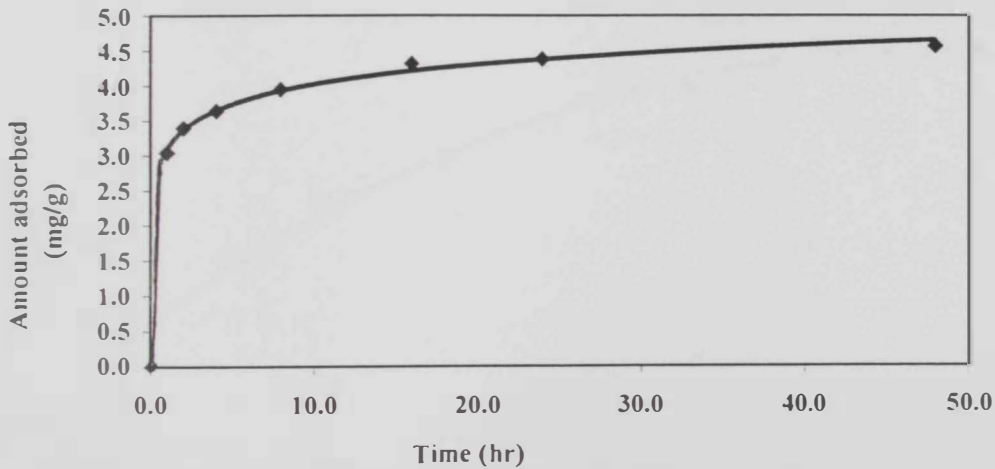


Figure 4-5 Adsorption rate of Phenol at different times onto PDKAC at 25°

4.7 Adsorption Isotherm

Adsorption under equilibrium conditions was determined for each of the phenol, aniline and methylene blue solutions. Figures 4.6, 4.7 and 4.8 depict the adsorption isotherms measured at 25 °C.

The adsorption characteristics depend primarily on the affinity of the solutes for the adsorbent material. In this study, the PDKAC was found to have higher selectivity for adsorbing phenol > aniline > methylene blue.

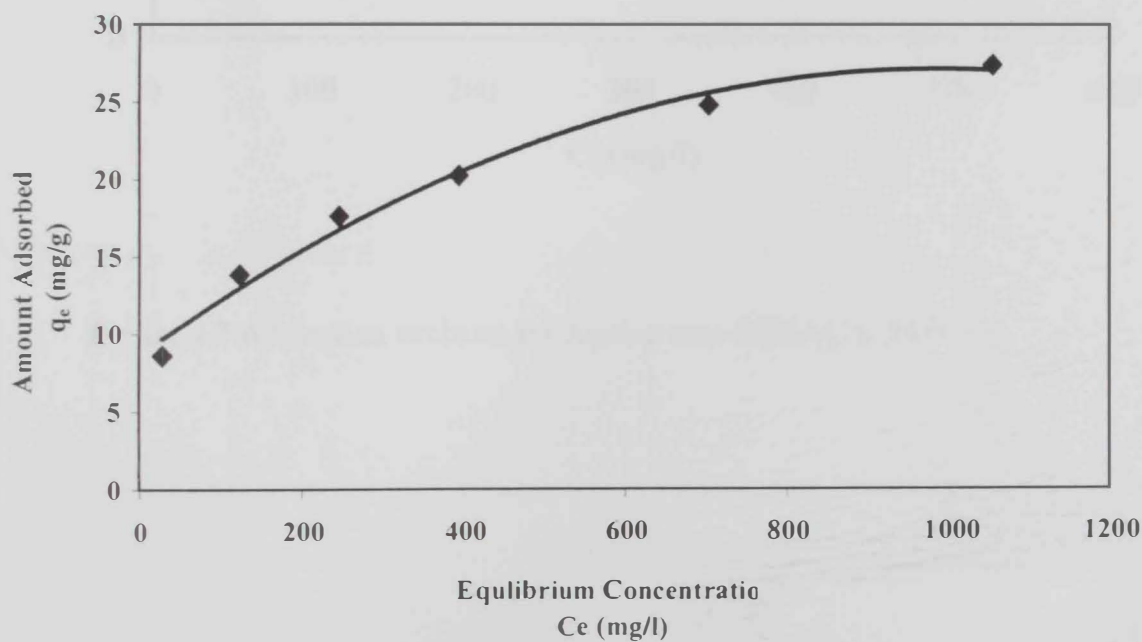


Figure 4.6 Adsorption isotherm for Phenol onto Palm Date Kernel Activated Carbon at 25 °C.

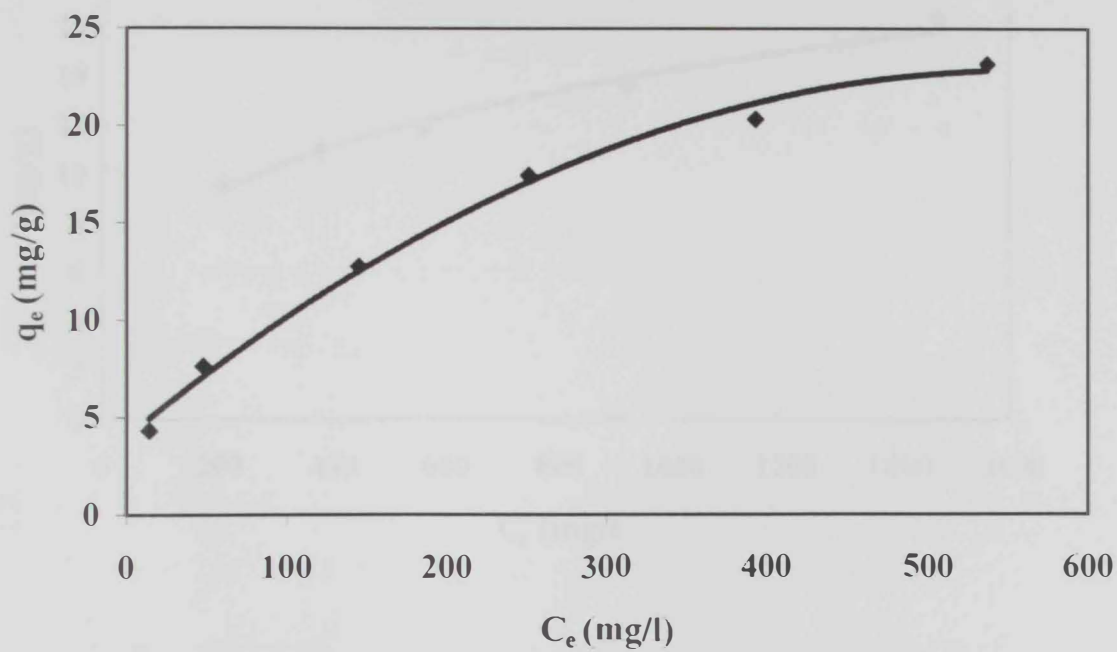


Figure 4.7 Adsorption isotherm for Aniline onto PDKAC at 25 °C.

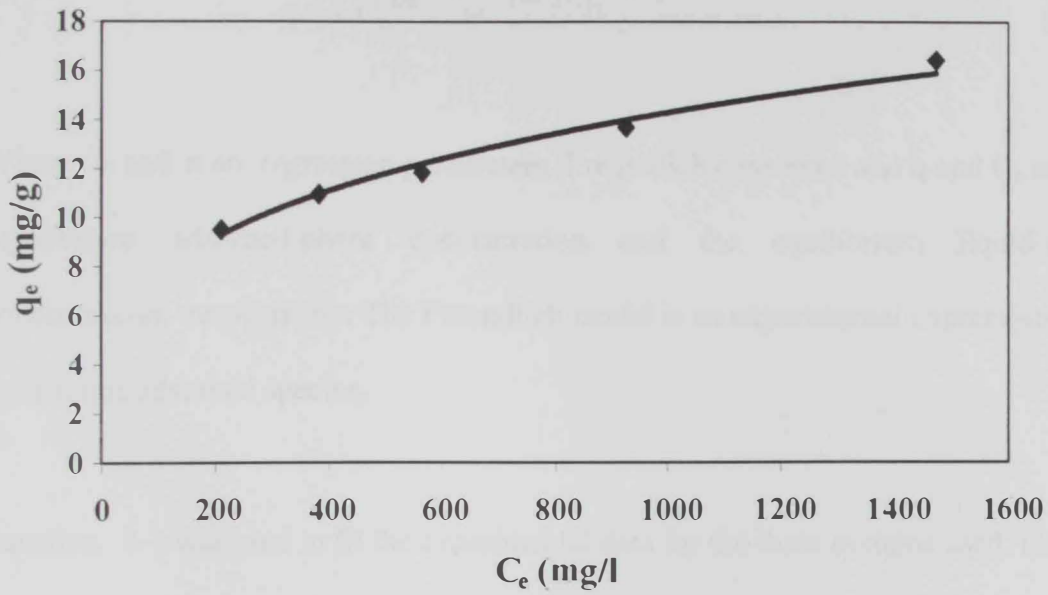


Figure 4.8 Adsorption isotherm for Methylene Blue onto PDKAC at 25 °C.

4.8 Analysis of Adsorption Isotherms

4.8.1 Freundlich Isotherms

Of more practical use in industry and easier to handle is the Freundlich isotherm equation, i.e.

$$q = k C_e^{1/n} \quad (4-1)$$

Where: **k** and **n** are regression parameters (Freundlich constants) and **q** and **C_e** are the equilibrium adsorbed-phase concentration and the equilibrium liquid-phase concentration, respectively. The Freundlich model is an experimental expression used for a single adsorbed species.

Equation 4-1 was used to fit the experimental data for the three systems used. Figures 4-9, 4-10, and 4-11 show the linear plots of $\log q_e$ versus $\log C_e$ obtained for each system (phenol, aniline and methylene blue), indicating the applicability of the Freundlich model. The regression parameters **k** and **n** for the Freundlich adsorption isotherm equation obtained for the three systems are listed in Table 4-4.

Table 4-4 Freundlich parameters for the adsorption of Phenol, Aniline and Methylene Blue.

| | <i>k</i> | <i>n</i> | <i>R</i> ² |
|-----------------------|----------|----------|-----------------------|
| <i>Phenol</i> | 2.93 | 3.09 | 0.9993 |
| <i>Aniline</i> | 1.26 | 2.14 | 0.9986 |
| <i>Methylene Blue</i> | 2.13 | 3.63 | 0.9835 |

According to the calculated “k” parameters, the selectively order for PDKAC adsorption is phenol > methylene blue > aniline.

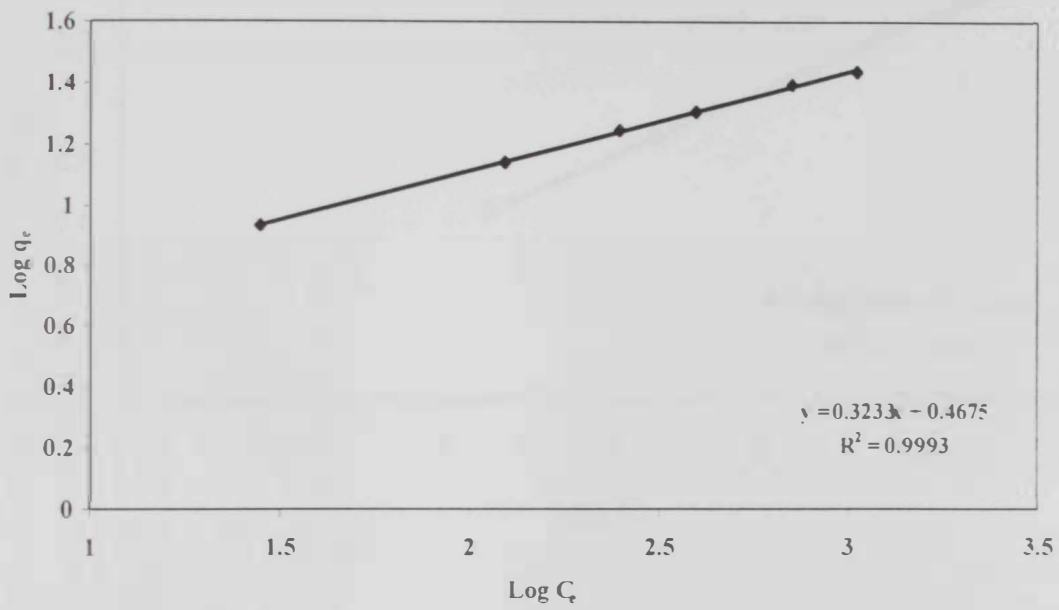


Figure 4-9 Freundlich isotherm for Phenol at 25 °C

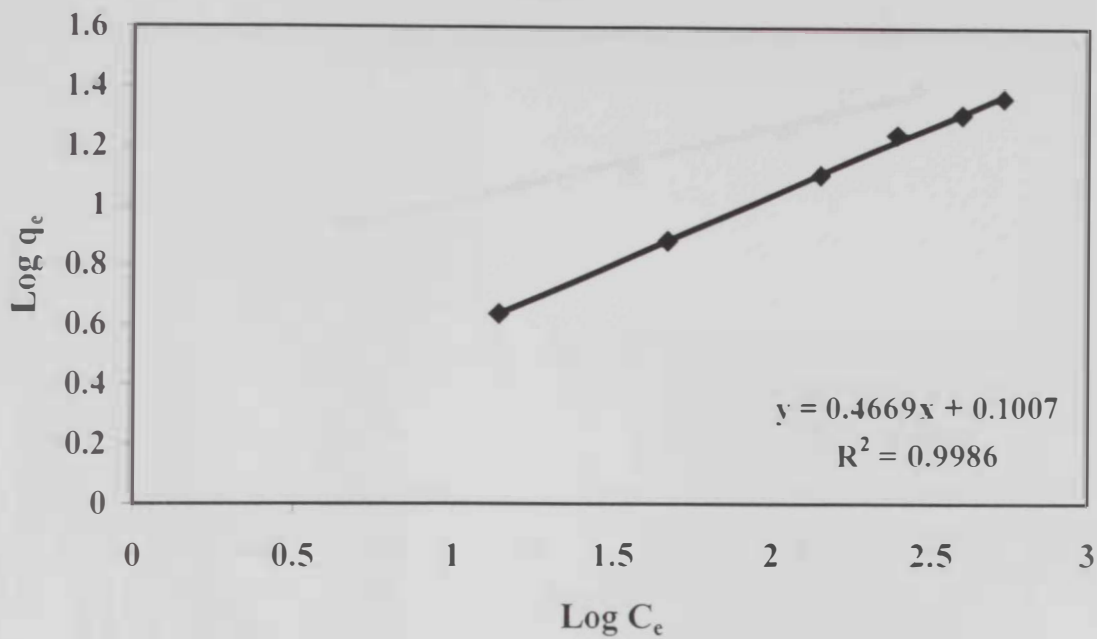


Figure 4-10 Freundlich isotherm for Aniline at 25 °C

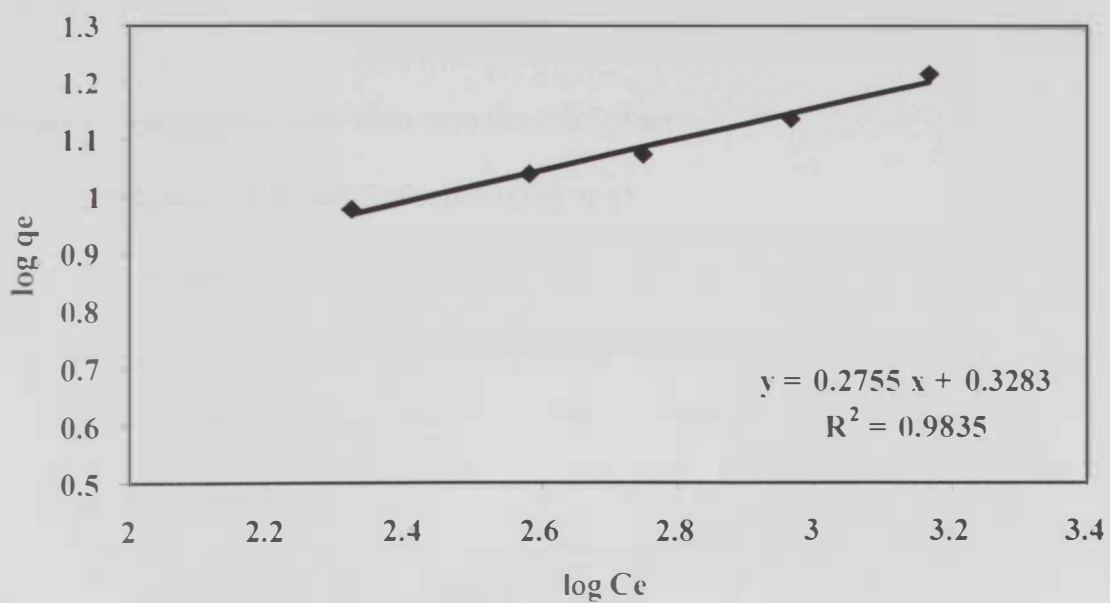


Figure 4-11 Freundlich isotherm for Methylene Blue at 25 °C

4.8.2 Langmuir Isotherm

The single-component Langmuir isotherm is one of the most popular two-parameter isotherm equations. The Langmuir isotherm has the following form:

$$q = x/m = (a b C_e)/(1 + a C_e) \quad (4.2)$$

Where q = adsorption mass ratio onto the solid phases

x = amount of material adsorbed (mg or g)

m = weight of adsorbent (mg or g)

C_e = concentration of material remaining in solution after adsorption is complete (mg/l).

a, b = constants

Taking the reciprocal of both sides of equation (4.2) yields:

$$1/q = (1/b) + (1/a b C_e) \quad (4.3)$$

If $1/q$ is plotted versus $1/C_e$, a straight line should be obtained over the region in which the Langmuir equation applies. This line will have a slope of $1/ab$ and an intercept of $1/b$. The experimental data for the systems were found to fit equation (4.3) as shown in Figures 4-12, 4-13, and 4-15. The Langmuir parameters for phenol, aniline, and methylene blue are shown in Table 4-5.

Table 4-5 Langmuir parameters for the adsorption of Phenol, Aniline and Methylene Blue Solutions.

| | <i>a</i> | <i>b</i> | <i>R</i> ² |
|-----------------------|----------|----------|-----------------------|
| <i>Phenol</i> | 0.0071 | 28.985 | 0.9704 |
| <i>Aniline</i> | 0.0088 | 25.381 | 0.9815 |
| <i>Methylene Blue</i> | 0.00612 | 16.34 | 0.9983 |

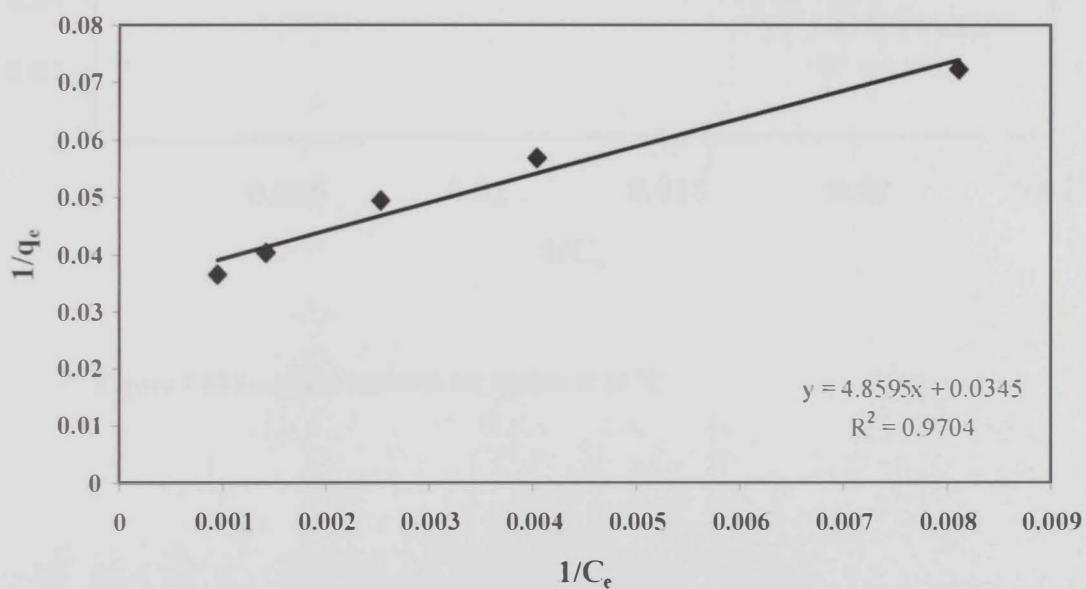


Figure 4-12 Langmuir isotherm for Phenol at 25 °C

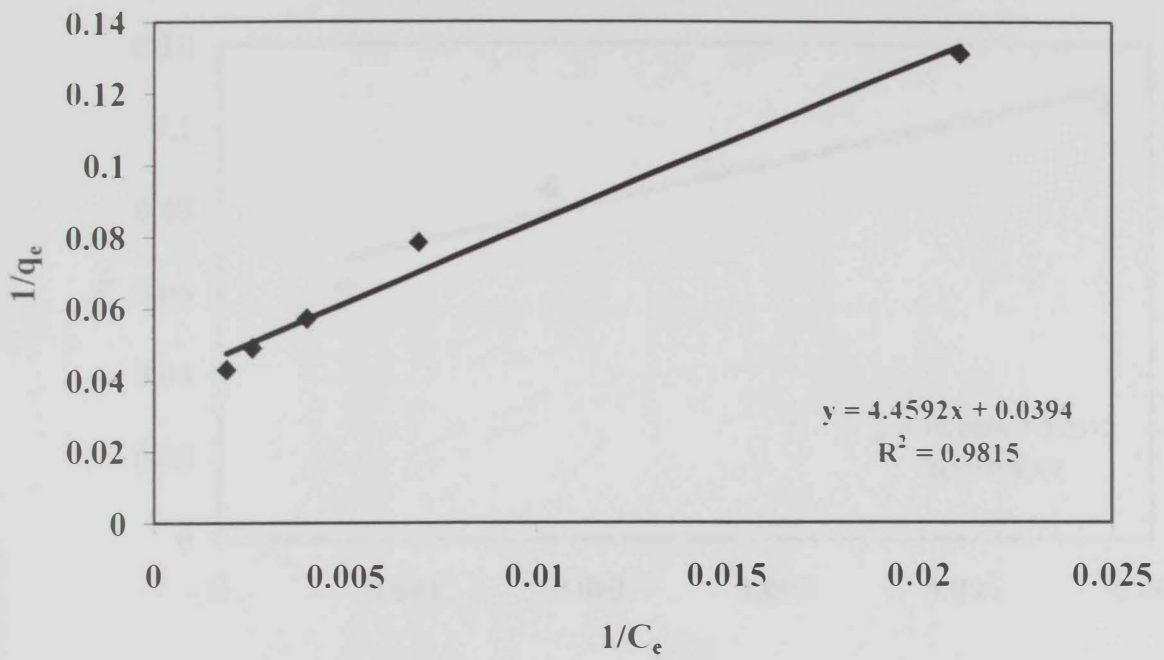


Figure 4-13 Langmuir isotherm for Aniline at 25 °C

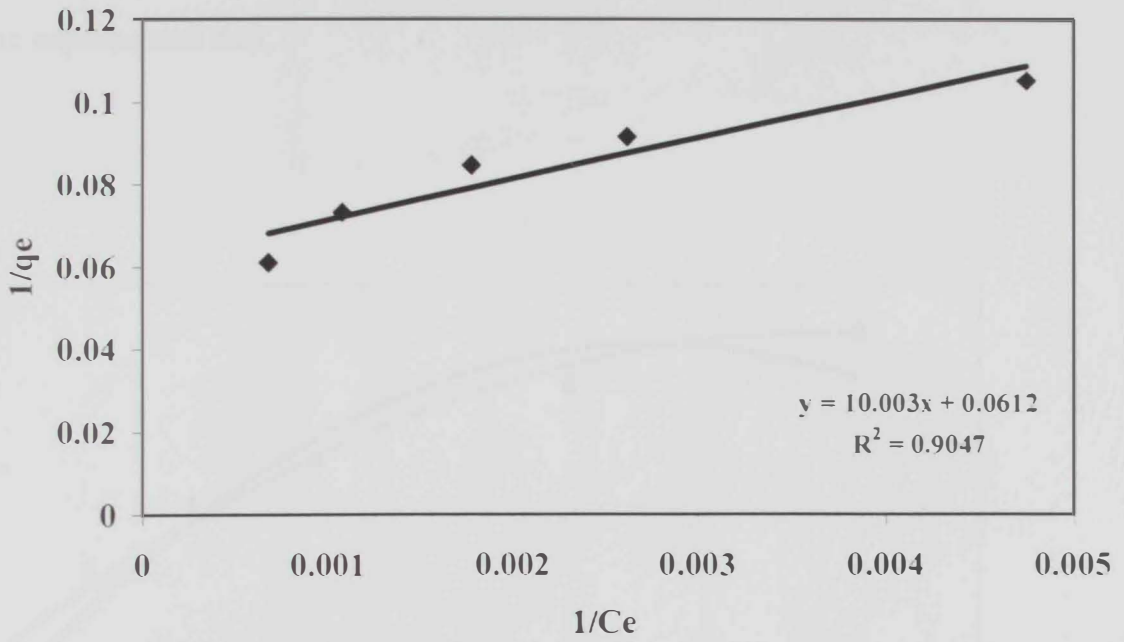


Figure 4-14 Langmuir isotherm for Methylene Blue at 25 °C

4.8.3 Comparison of Models

The previous model analysis can be summarized as shown in Figures 4-15, 4-16, and 4-17, for highlighting the possible differences between the predicted values and experimental data. The Figures clearly indicate that the used models fit very well the obtained experimental data.

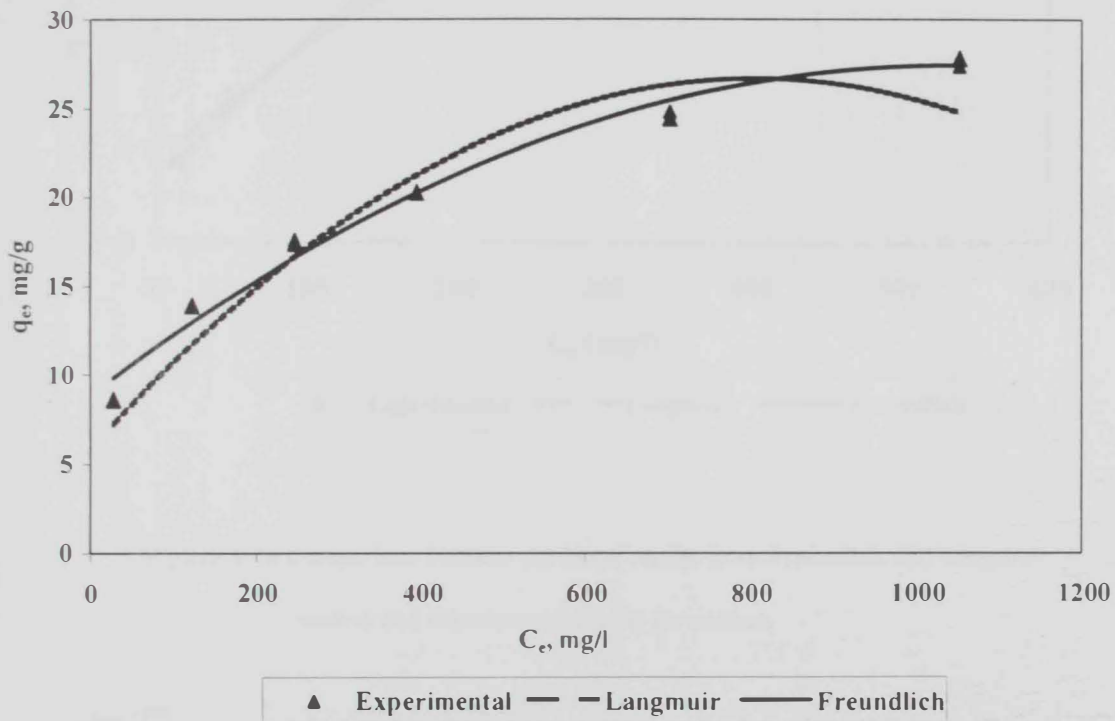


Figure 4-15 Comparison between predicted results from Freundlich & Langmuir models and experimental results for phenol.

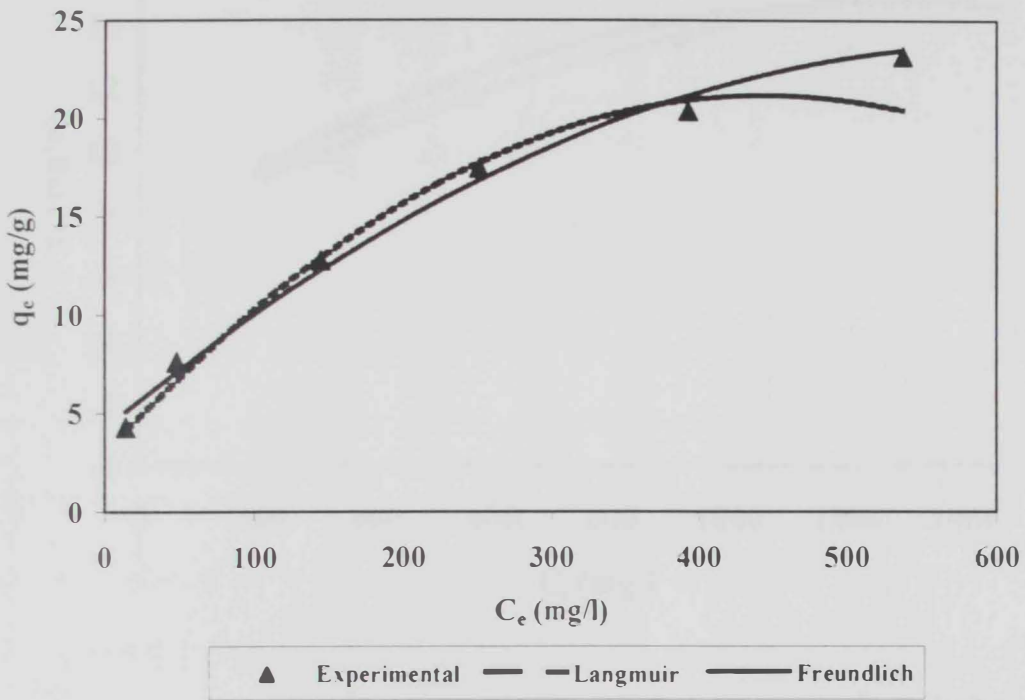


Figure 4-16 Comparison between predicted results from Freundlich and Langmuir models and experimental results for aniline.

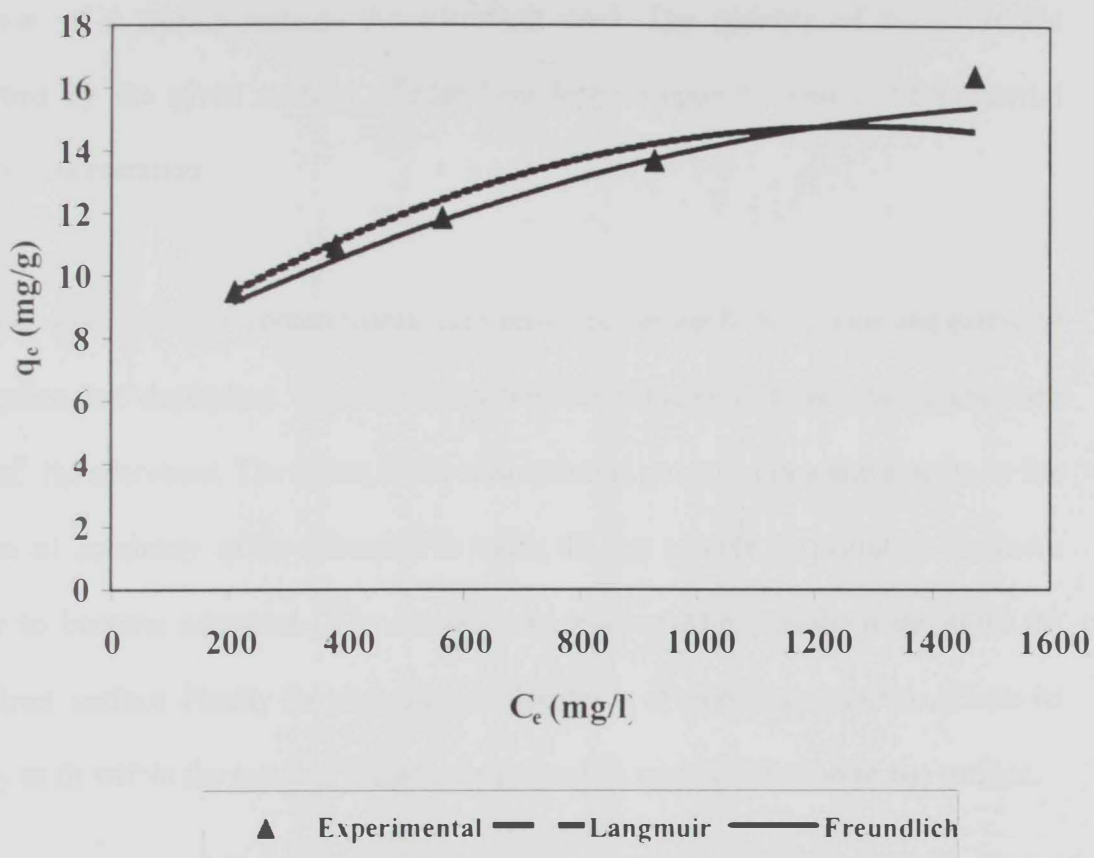


Figure 4-17 Comparison between predicted results from Freundlich and Langmuir models and experimental results for methylene blue.

4.8.4 Possible Adsorption Mechanisms.

Since adsorption is a surface phenomena the rate and extent of adsorption is a function of a surface area of the adsorbent used. The quantity of the substance adsorbed by the given sample of adsorbent depends upon the nature of the material and its concentration

For the adsorption of contaminants into activated carbon both the rate and extent of adsorption are dependent upon the characteristics of the contaminant being adsorbed and of the adsorbent. The extent of the adsorption is governed to some extents by the degree of solubility of the substance in water, the less soluble the pollutant the more likely to become adsorbed. The second is the relative affinity of the material for the adsorbent surface. Finally the size of the molecules is of significance as this effects its ability to fit within the pores of the adsorbents and its rate of diffusion to the surface.

The difference in the adsorption characteristics observed from the isotherms of the different adsorbate used for the study can be attributed to the chemical structure and sizes of the adsorbate. The chemical structure of phenol, aniline, and methylene blue is given in Figure 4-18, 4-19, and 4-20. Also the functional groups of the compounds play a significant role in the adsorption capacity of the compound.

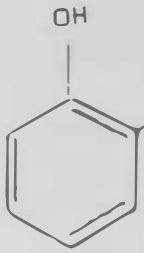


Figure 4-18 The chemical structure of phenol



Figure 4-19 The chemical structure of aniline

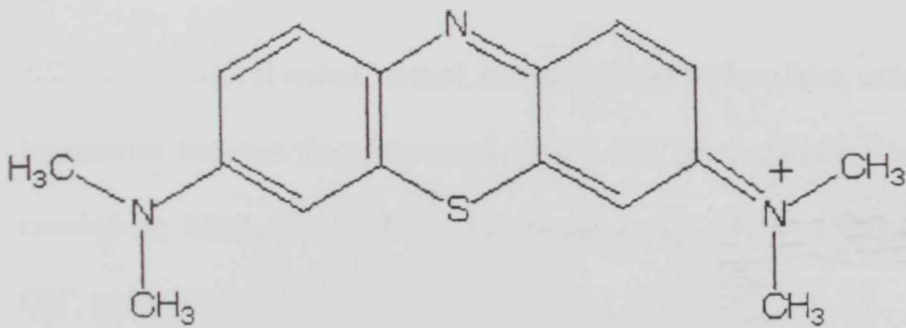


Figure 4-20 The chemical structure of methylene blue

The possible interaction mechanisms are:

1. **Water Bridging:** This involves complexation with a water molecule. For example, the carboxylate groups in humic substances associate with PDKAC through cation bridging when monovalent exchangeable cations are present and through water bridging when bivalent exchangeable cations are present.

Among the three chemicals tested, phenol exhibits this type of interaction between its OH^- group and the surface functional group of the PDKAC, COOH^- , C=O , N=O^- , OH^- , and CH^- .

2. **van der Waals Interactions:** For polymeric humus material, the van der Waals interactions with the atoms in the mineral surface can be quite strong and relatively long-ranged. The effects of van der Waals interactions are apparent when conditions in the PDKAC suppress the ionization of acidic functional groups on large organic molecules.

All three chemical tested, phenol, aniline, and methylene blue, exhibit this type of interaction between their functional groups, OH^- (phenol), NH_2 (aniline), and CH_3 (methylene blue), and PDKAC functional groups N^+H , COOH^- , C=O , N=O^- , OH^- , and CH^- .

3. *Weak Hydrogen Bonding:* This occurs between organic functional groups and PDKAC. It does not appear to be significant in humus reactions with PDKAC, probably because the electro-negativity of mineral surface oxygen usually is not large enough to form strong H bonds.

All three chemical tested, phenol, aniline, and methylene blue, exhibit this type of interaction between their functional groups, OH⁻ (phenol), NH₂ (aniline), and CH₂ (methylene blue, and PDKAC functional groups N⁺H⁻, COOH⁻, C=O⁻, N=O⁻, OH⁻, and CH⁻).

The most definitive method for establishing the formation of a chemical bond between the adsorbing molecule and the substrate (i.e. chemisorption) is to use an appropriate spectroscopic technique, for example, IR to observe the vibrational frequency of the substrate/adsorbate bond.

CHAPTER 5

SUMMARY & CONCLUSIONS

CHAPTER 5

SUMMARY & CONCLUSIONS

There has been a growing interest worldwide to employ cost-effective treatment methods for polishing secondary treated wastewater effluents. Activated carbon adsorption has proved to be an effective method for effluent polishing but treatment costs are relatively high. For this purpose Palm Date Kernels could be activated and used to remove trace contaminants from treated effluents, as a cost-effective material and easily available in the United Arab Emirates and Gulf region. This must be investigated and the results of the study can be helpful in developing an economically viable method. If recommended water quality standards can be met, the treated water can be utilized for other municipal, industrial and agricultural purposes.

Removal of trace contaminants from wastewater effluent using local adsorbents has been investigated using adsorption techniques. Palm Date Kernel Activated Carbon (PDKAC), a locally made adsorbent, has been used for the adsorption of compounds (phenol, aniline, methylene blue) in batch tests at 25 °C and adsorbent particle size $\leq 75 \mu\text{m}$.

The adsorbent (PDKAC), was prepared by using the dry date kernels, which are subjected to pyrolysis process, then it is grounded and sieved, the palm date kernel carbonizate particles were then subjected to a steam activation process, finally washed several times with deionized water and dried.

The equilibrium time was conducted by using phenol solution at different time. The experimental data showed that the amount adsorbed has increased with time at constant temperature of 25 °C, reaching equilibrium after 24 hrs.

The experimental results showed that the selectivity of adsorption by PDKAC is phenol > aniline > methylene blue. The experimental isotherm data were fitted to both Freundlich and Langmuir models.

The results revealed the potential use of PDKAC as a low-cost adsorbent. Furthermore, the results indicated that the PDKAC could be utilized effectively in the removal of trace contaminants from wastewater effluent as well as decoloring of solutions.

The developed material has a very high potential use in industry to compat various problems related to pollution of organic chemical.

Recommendation for Future Study

The study revealed that activated carbon produced from locally available raw material (PDKAC) has the ability to remove partially the selected adsorbate from water. With the current practice of using chlorine as a disinfectant for wastewater effluent, there is always the possibility of the formation of trihalomethanes (THMs).

It would be beneficial if adsorption studies are conducted using PDKAC and chlorinated effluent to see the potential of using PDKAC as an adsorbent for the removal of hazardous by-product of chlorination.

It is also recommended to carry out comparative studies with commercially available carbon to see the efficiency and cost effectiveness of using PDKAC. If it is economically feasible and cost effective, then steps are to be taken to commercially produce activated carbon on a large scale.

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APPENDIX

APPENDIX

Table A-1 Adsorption rate of Phenol at different times

| Time, hrs | Amount of Phenol before Adsorption, mg | Instrument Response | Concentration after Adsorption (C_e), mg/l | Amount after Adsorption, mg | Amount of Phenol Adsorbed (q_e), mg/g of carbon |
|-----------|--|---------------------|--|-----------------------------|---|
| 0 | 5.0000 | | 100.0000 | 5.0000 | 0.0000 |
| 1 | 5.0000 | 0.5810 | 39.1892 | 1.9595 | 3.0405 |
| 2 | 5.0000 | 0.4760 | 32.0946 | 1.6047 | 3.3953 |
| 4 | 5.0000 | 0.4040 | 27.2297 | 1.3615 | 3.6385 |
| 8 | 5.0000 | 0.3130 | 21.0811 | 1.0541 | 3.9459 |
| 16 | 5.0000 | 0.2030 | 13.6486 | 0.6824 | 4.3176 |
| 24 | 5.0000 | 0.1850 | 12.4324 | 0.6216 | 4.3784 |
| 48 | 5.0000 | 0.1280 | 8.7823 | 0.4391 | 4.5609 |

Table A-2 Adsorption isotherm and Freundlich & Langmuir isotherms data of Phenol

| C_e , mg/l | q_e , mg/g | $1/C_e$ | $1/q_e$ | $\text{Log } C_e$ | $\text{Log } q_e$ |
|--------------|--------------|-----------|-----------|-------------------|-------------------|
| 28.0268 | 8.5987 | 0.0356801 | 0.1162966 | 1.4475735 | 0.9344328 |
| 123.2215 | 13.8389 | 0.0081155 | 0.0722601 | 2.0906865 | 1.1411016 |
| 247.3826 | 17.6309 | 0.0040423 | 0.0567186 | 2.3933691 | 1.2462745 |
| 395.0336 | 20.2483 | 0.0025314 | 0.0493869 | 2.596634 | 1.3063886 |
| 704.0268 | 24.7987 | 0.0014204 | 0.0403247 | 2.8475892 | 1.3944289 |
| 1052.349 | 27.3826 | 0.0009503 | 0.0365195 | 3.0221598 | 1.4374747 |

Table A-3 Adsorption isotherm and Freundlich & Langmuir isotherms data of Aniline

| C_e , mg/l | q_e , mg/g | $1/C_e$ | $1/q_e$ | $\text{Log } C_e$ | $\text{Log } q_e$ |
|--------------|--------------|---------|---------|-------------------|-------------------|
| 13.9595 | 4.302 | 0.07164 | 0.23245 | 1.14487 | 0.63367 |
| 47.5135 | 7.6243 | 0.02105 | 0.13116 | 1.67682 | 0.8822 |
| 144.797 | 12.7601 | 0.00691 | 0.07837 | 2.16076 | 1.10585 |
| 251.081 | 17.4459 | 0.00398 | 0.05732 | 2.39981 | 1.24169 |
| 392.905 | 20.3547 | 0.00255 | 0.04913 | 2.59429 | 1.30866 |
| 536.487 | 23.1757 | 0.00186 | 0.04315 | 2.72956 | 1.36503 |

Table A-4 Adsorption isotherm and Freundlich & Langmuir isotherms data for methylene blue

| C_e , mg/l | q_e , mg/g | $1/C_e$ | $1/q_e$ | $\log C_e$ | $\log q_e$ |
|--------------|--------------|---------|---------|------------|------------|
| 210.127 | 9.4937 | 0.00476 | 0.10533 | 2.32248 | 0.97744 |
| 381.288 | 10.9356 | 0.00262 | 0.09144 | 2.58125 | 1.03884 |
| 563.346 | 11.8327 | 0.00178 | 0.08451 | 2.75078 | 1.07308 |
| 926.362 | 13.6819 | 0.00108 | 0.07309 | 2.96678 | 1.13615 |
| 1471.66 | 16.4172 | 0.00068 | 0.06091 | 3.16781 | 1.2153 |

Table A-5 Comparison between predicted results from Freundlich and Langmuir models and experimental results for phenol.

| C_e, mg/l | q_e (experimental), mg/g | q_e (Langmuir), mg/g | q_e (Freundlich), mg/g |
|----------------------------|---|---------------------------------------|---|
| 28.0268 | 8.5987 | 4.81 | 8.62 |
| 123.2215 | 13.8389 | 13.53 | 13.91 |
| 247.3826 | 17.6309 | 18.47 | 17.43 |
| 395.0336 | 20.2483 | 21.37 | 20.276 |
| 704.0268 | 24.7987 | 24.15 | 24.44 |
| 1052.349 | 27.3826 | 25.6 | 27.833 |

Table A-6 Comparison between predicted results from Freundlich and Langmuir models and experimental results for aniline.

| C_e, mg/l | q_e (experimental), mg/g | q_e (Langmuir), mg/g | q_e (Freundlich), mg/g |
|----------------------------|---|---------------------------------------|---|
| 13.9595 | 4.302 | 2.8 | 4.32 |
| 47.5135 | 7.6243 | 7.48 | 7.66 |
| 144.797 | 12.7601 | 14.22 | 12.9 |
| 251.081 | 17.4459 | 17.48 | 16.68 |
| 392.905 | 20.3547 | 19.7 | 20.56 |
| 536.487 | 23.1757 | 21 | 23.78 |

Table A-7 Comparison between predicted results from Freundlich and Langmuir models and experimental results for methylene blue.

| C_e , mg/l | q_e (experimental), mg/g | q_e (Langmuir), mg/g | q_e (Freundlich), mg/g |
|--------------|----------------------------|------------------------|--------------------------|
| 210.127 | 9.4937 | 9.2 | 9.02 |
| 381.288 | 10.9356 | 11.4 | 10.63 |
| 563.346 | 11.8327 | 12.6 | 11.84 |
| 926.362 | 13.6819 | 13.9 | 13.575 |
| 1471.66 | 16.4172 | 14.7 | 15.42 |

Figure A-1 Calibration Curve of Phenol at 270 nm

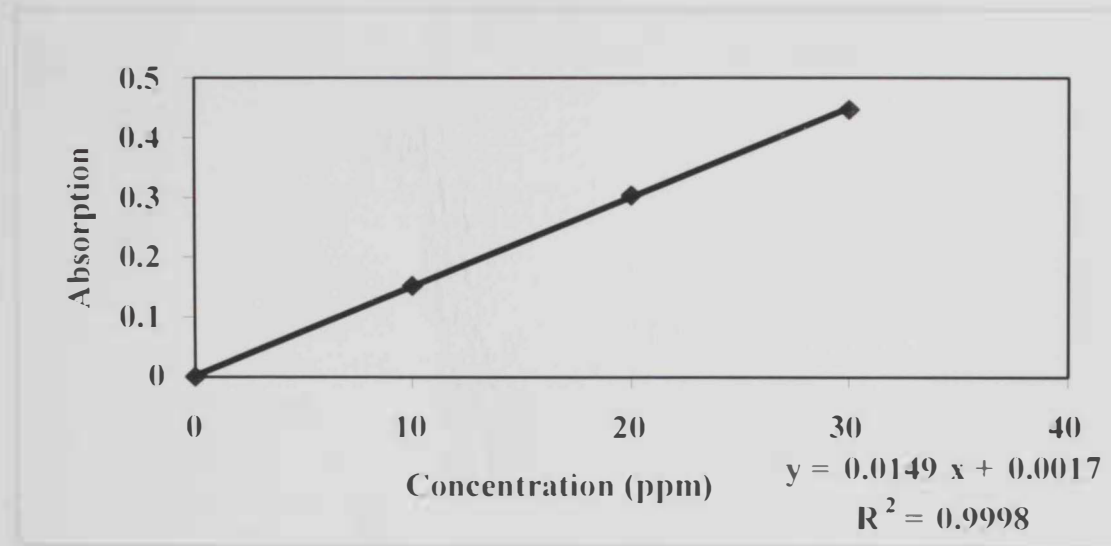


Figure A-2 Calibration Curve of Aniline at 280 nm

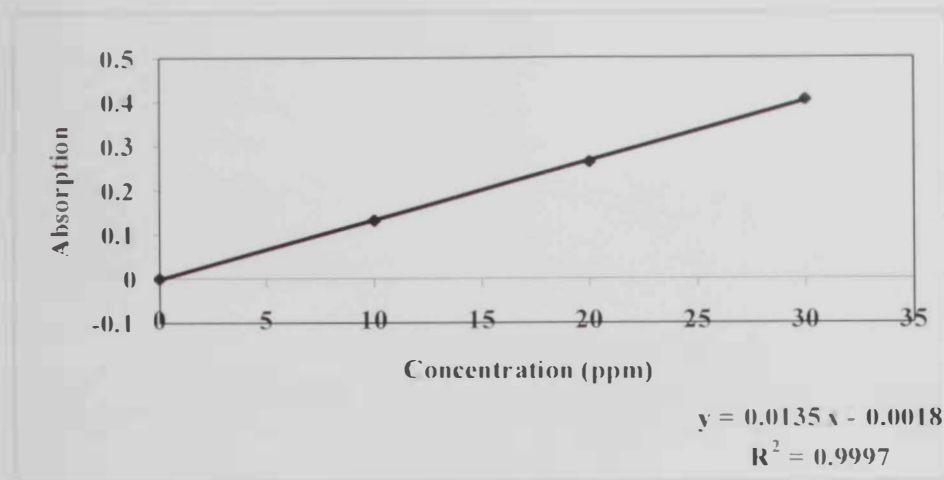
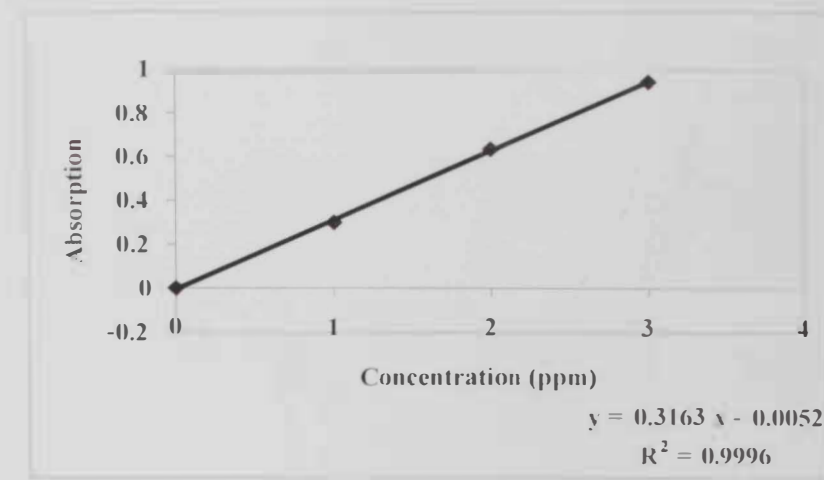


Figure A-3 Calibration Curve for Methylene Blue at 661 nm



إن الفرق في خواص المواد المدمصة يمكن أن يعزى إما إلى التركيب الكيميائي أو إلى حجم جزيئات الفينول والانيولين وصبغة المثلين الأزرق.

النتائج

أثبتت التجارب إن الامصاص يمكن أن يستخدم بنجاح في إزالة الملوثات الدقيقة. وإن الكربون المنشط يمكنه أدمصاص مركبات الفينول والانيولين والمثلين الأزرق في محطة المجاري بزاخر. وقد تم تحليل النتائج وفق نموذجين لكل من Freundlich و Langmuir حيث وجد إن هذه النماذج كافية للتعبير عن النتائج المخبرية.

إن استعمال الكربون المنشط المتوفر محليا سيؤدي إلى إيجاد طريقة فعالة ورخيصة في تنظيف المياه الناتجة عن عملية التنقية. وبالتالي تتحسن نوعية هذه المياه التي يعاد استعمالها في الري.

تجهيز الكربون المنشط

إن الكربون المنشط من نوع البلح PDKAC والذي يجهز محليا كمادة مدمصة. هذه المادة استعملت لإدمصاص مركبات الفينول والانيلين و صبغة الميثيلين الأزرق وذلك خلال مجموعة من التجارب والاختبارات حيث أظهرت قدرتها على أدمصاص مركبات الفينول والانيلين وصبغة الميثيلين الأزرق عند درجة الحرارة 25°C فقامت بإدمصاص الجزيئات ذات حجم ≥ 75 ميكرومتر فكشفت النتائج عن مقدرة كافية للكربون المنشط في أدمصاص المركبات سالفة الذكر، علاوة إن الكربون من نوع البلح غير مكلف اقتصاديا، وقد دلت التجارب على إن الكربون المنشط أظهر قدرة استيعابية أكبر في أدمصاص مركبات الفينول وصبغة الميثيلين الأزرق أكثر من مركب الانيلين، و قد تم ثبات نتائج الاختبارات حسب نموذجين لكل من Langmuir و Freundlich لأن القيم أوضحت إن مركبات الفينول والانيلين وصبغة الميثيلين الأزرق تميل نحو الأدمصاص على الكربون المنشط.

التجربة

تم جمع نوى البلح من مدينة العين بدولة الإمارات العربية المتحدة حيث تم معاملة النوى حراريا عند درجة الحرارة 750°C في غياب الهواء لمدة 8 ساعات. بعد ذلك تم طحن فحم النوى إلى أقل حجم ممكن ثم مرر منخل عند قطر ≥ 75 ميكرومتر. ثم تم تنشيط فحم النوى بواسطة البخار عند درجة الحرارة 750°C لمدة 8 ساعات، ثم غسلت جزيئات الكربون المنشط باستعمال ماء مقطر ولعدة مرات وذلك لإزالة الشوائب الذائبة ثم يجفف الكربون لا هوائيا عند درجة حرارة 200°C لمدة يوم كامل ثم يوضع في المجففة.

تم إضافة 50 ملل من كل من المحاليل الفينول والانيلين وصبغة الميثيلين الأزرق إلى (1 جم) من الكربون المنشط (PDKAC) في قناني سعة 100 ملل منفصلة ثم وضعت على جهاز الرج لفترة كافية من الزمن للتأكد من الاتزان قد تحقق. النتائج التجريبية الأولية أظهرت إن الاتزان تحقق في خلال 24 ساعة، بعد تلك الفترة تؤخذ القناني ويتم عملية فصل الكربون عن المحلول بواسطة ورق مصفى وتؤخذ التقدير تركيز الاتزان، ولغرض بين التركيز الابتدائي والتركيز بعد الاتزان استخدم لحساب كمية الفينول أو الانيلين أو صبغة الميثيلين الأزرق من المحلول. وقد تم إجراء جميع التجارب عند درجة الحرارة 25°C وذلك لمنع أي تأثير لدرجات الحرارة.

ملخص الرسالة

مخوان الأطروحة

ازالة الملوثات الدقيقة من مياه المجاري المعالجة باستخدام
كربون منشط (نوى البلح) محلي.

إن أي معالجة لمياه مجاري يجب أن يتم فيها التخلص من الملوثات المتبقية بدرجات عالية
وذلك لجعل هذه المياه مقبولة عند إعادة استعمالها. وهناك اهتمام متزايد في جميع أنحاء العالم
بأنعمال طرق معالجة مؤثرة لتنقية النواتج الثانوية لمياه المجاري. ومن هذا المنطلق استخدم
الكربون كمادة مدمصة، وقد أثبتت التحارب فاعلية هذه الطريقة في تنظيف الناتج النهائي ولكنها
مكلفة مالياً.

إن محطة تنقية مياه المجاري لمدينة العين الواقعة بمنطقة زاهر والتي تبلغ طاقتها الاستيعابية
(٥٤,٠٠٠ م^٣ في اليوم)، هذه المحطة تقوم بالمعالجة الأولية لمياه المجاري ثم تعقبها عملية
التجوية وترشيح للندج النهائي الذي يعاد استخدامه في أغراض الري.

إن المواصفات الكيميائية للمياه المعالجة في محطة التنقية بزاهر تم تقديرها، وأهم ما فيها هي
الملوثات العضوية الدقيقة والتي تؤثر عكسياً على نوعية وملانمة هذه المياه لإعادة الاستعمال.
وبعد تحديد كمية الملوثات الكيميائية أصبح من الضروري تحديد الطرق الكافية لزيادة تنظيف
المياه الناتجة عن عملية التنقية باستعمال المواد المدمصة والمتوفرة محلياً. لأجل هذا الغرض
يمكن استعمال نوى البلح الموجود محلياً بكثرة في أشجار النخيل وذلك بعد تنشيطه ليقوم
بامتصاص الملوثات العضوية الموجودة في الناتج النهائي لمياه المجاري المعالجة في محطة
التنقية. وهذا الأمر يجب أن يدرس ونتائج الدراسة والبحث يمكن أن تكون مفيدة في تطوير
طريقة اقتصادية لإزالة الملوثات المتبقية في المجاري الناتجة بعد التنقية، وإذا تم الحصول على
مياه ذات نوعية قياسية فإنه في هذه الحالة يمكن استعمال هذه المياه للأغراض الزراعية
والصناعية.

ملخص العربي

الملخص العربي

إزالة الملوثات الدقيقة من مياه المجاري المعالجة باستخدام كربون منشط
(نوى الباج) محلي

قاسم غلام حيدر غلام

(رسالة مقدمة إلى كلية العلوم بجامعة الإمارات العربية المتحدة
إيفاء جزئياً لمتطلبات نيل درجة الماجستير في علوم البيئة)

كلية العلوم
جامعة الإمارات العربية المتحدة
(يونيو - ١٩٩٩)