REMOVAL OF PHENOL FROM AQUEOUS SOLUTION BY DRIED WATER HYACINTH *(Eichhornia Crassipes)*

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ABSTRACT

This potential of dried water hyacinth for phenol adsorption from aqueous solution was studied. The objective in this study is to study the removal of phenol from aqueous solution by dried water hyacinth. Four parameters in this study are effect of initial phenol concentration, dried water hyacinth dosage, pH and contact time. Phenol is very harmful even at low concentration and very hazardous chemical because of their potential toxicity to human health. Adsorption is one of the best methods to remove phenol because of economical and safe process. It is a relatively new process that has been proven very promising in the removal of contaminants from aqueous effluents. Water hyacinth is the suitable adsorbent to remove phenol from aqueous solution. It is very easily available and one of the low cost adsorbent. We used dried to avoid the spreading of dengue fever to the residents nearby and easily to handle and keep it. To conduct this study, first method is collect the water hyacinth. Then, prepare the adsorbent and stock solution. After that, run the experiment for each parameter and lastly analyze the sample. The analysis was done by using UV-Vis Spectrophotometer. From the result obtained, we know that the removal of phenol ions was optimum when initial phenol concentration was almost 70 mg/ L, adsorbent dosage at 1.8 g, pH 3 and at 3 hours contact time. From this study, it is shows that a biomaterial produced from dried water hyacinth can provide a simple, effective and yet cheaper method in removing phenol from aqueous solution.

ABSTRAK

Kajian ini membentangkan hasil ujikaji tentang kebolehan keladi bunting untuk menjerap phenol dalam larutan cecair.. Objektif dalam ujikaji ini adalah mengkaji penyingkiran phenol dari larutan cecair dengan menggunakan keladi bunting kering. Pembolehubah dalam ujikaji ini adalah kesan dos penjerap, kepekatan awal larutan phenol, pH dan masa bersentuhan. Phenol amat merbahaya walaupun dalam kepekatan yang rendah disebabkan ketoksidannya Penjerapan adalah satu process yang bagus untuk menyingkirkan phenol kerana process ini murah dan selamat. Keladi bunting adalah bahan penjerap yang sesuai digunakan untuk menyingkirkan phenol dari larutan cecair. Ia banyak dan senang diperolehi. Kami menggunakan keladi bunting yang dikeringkan adalah untuk mengelakkan pemerebakan demam denggi di kawasan berdekatan dan senang untuk dikawal dan disimpan. Untuk menjalankan ujikaji ini, langkah pertama adalah memungut keladi bunting. Kemudian, sediakan bahan penjerap dan stok larutan. Selepas itu, jalankan eksperimen untuk setiap pembolehubah dan akhir sekali adalah menganalisis sampel dengan menggunakan UV-Vis Spectrophotometer. Daripada keputusan yang diperolehi, penyingkiran phenol adalah optimum apabila kepekatan awal phenol adalah 70 mg/l, dos bahan penjerap adalah 1.8 gram, pH larutan phenol adalah 3 dan masa bersentuhan adalah 3 jam. Ujikaji ini telah menunjukkan keladi bunting boleh menyediakan kaedah yang ringkas, berkesan dan murah untuk menyingkirkan phenol dari larutan cecair.

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LIST OF SYMBOLS

C_6H_5OH	-	Phenol
Na_2CO_3	-	Sodium Carbonate
$C_6H_5O^-$	–	Phenolate ion
HCL	-	Hydrocloric acid
NaOH	-	Natrium Hydroxide
H^+	-	Hydrogen ion
OH^-	-	Hyrdoxyl
g	-	gram
min	-	minutes
hr	-	hour
kg	-	kilogram
V	-	Volume
W	-	Weight
Ppm	-	part per million
mg/L	-	milligrams per liter
mL	-	mililitre
rpm	-	revolution per minute
µm	-	micro metre
*C*i	-	initial concentration
*C*e	-	equilibrium concentration
*Q*e	-	uptake capacity
FTIR	-	Fourier Transform Infrared
EPA	-	Environmental Protection Agency
BOD	-	Biological Oxygen Demand
UMP	-	University Malaysia Pahang
R&D	-	Research and Development
^oF	-	degree Fahrenheit
^oC	-	degree Celcius

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Pollution is the release of chemical, physical, biological or radioactive contaminants to the environment. Water pollution is one of the most serious problems of today's civilization. It affects oceans and inland bodies of water. Among pollutant for water includes organic and inorganic chemicals, heavy metals, petrochemicals, chloroform, and bacteria. Water pollution may also occur in the form of thermal pollution and the depletion of dissolved oxygen.

Pollutants present in trace amounts in wastewater may have several short and long terms effect on the flora and fauna as well as on the human health (Kaustubha Mohanty *et al*., 2008).They include poisonous of drinking water, poisonous of food animals, unbalanced river and lake ecosystem and also can cause diseases, including cancer, immune diseases, allergies, and asthma. Higher levels of background radiation have led to an increased incidence of cancer and mortality associated with it worldwide.

Phenols are one of the direct contaminants that will cause the water pollution. Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential to harm human health. Because of their toxicity, phenols have been

included in the of US Environmental Protection Agency (EPA) list of priority pollutants (N. Calace *et al*., 2002).

Phenols are generated from oil, gasoline, coal, paper, textile, petroleum, petrochemicals, pharmaceuticals, phenol producing industries and plants, which are processing phenols to plastics. The concentration of phenol compounds in the aqueous solution from resin plants is typically in the range of 12 - 300 mg/L. The aqueous solution with the highest concentration of phenol (> 1000 mg/L) is typically generated from coke processing. Ingestion of a small amount of phenol (TLV of 5 ppm) by human beings may cause nausea, vomiting, paralysis, coma, greenish or smoky colored urine and even death from respiratory failure or cardiac arrests (Atef S. Alzaydien *et al*., 2009). Thus, the removal of such chemicals from industrial effluents is of great importance (S. Rengaraj *et al*., 2002).

There are a lot of methods that can be used to remove phenol from aqueous solution like adsorption, microbial degradation, chemical oxidation, precipitation, ion change, solvent extraction and many more for removing phenols and its derivatives from aqueous solutions. Amongst these, adsorption is considered to be the most potential one due to its high efficiency and ability to separate wide range of chemical compounds (H. Cherifi *et al*., 2008). Adsorption is a consequence of attractive interactions between the surface of the adsorbent and the species being adsorbed. Impurities or contaminants are filtered from liquids or gases by adsorption onto adsorbents.

Activated carbon is one the most effective adsorbents for organic compounds, as it has a high surface area per unit mass and exhibits a high adsorption capacity for phenol compounds (N. Calace *et al*., 2002). However, due to the relatively high cost of activated carbon it has been attempted to utilize low cost, naturally occurring adsorbents to remove phenol from aqueous solution.

There are some new adsorbents that can be used to remove phenol from aqueous solution such as water hyacinth, fly ash, peat, soil, rice husk and activated sludge. Among them, water hyacinth is very suitable adsorbent to remove phenol from aqueous

solution. Water hyacinths are aquatic plant that available and easy to get especially in our country. It also can be used as a cost effective adsorbent for the removal of phenol from aqueous solution. This floating perennial has been used in aquatic systems for wastewater purification for many years worldwide and very efficient in removing vast range of pollutants, from suspended materials, BOD, nutrients, organic matter to heavy metals and pathogens. Water hyacinth can become adsorbent in two form which is in aquatic or dried. Compare to dried and aquatic water hyacinth, dried water hyacinth is commonly used.

1.2 PROBLEM STATEMENT

Organic contaminants from industrial waste streams that seriously threaten the human health and the environment have been recognized as an issue of growing importance in recent years. Phenol pollution is a serious problem in many countries (Atef S. Alzaydien *et al*., 2009). Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health. Phenol that discharges from any factories into waterways will adversely affect human health as well as that of flora and fauna. The ingestion of such contaminated water in the human body causes protein degeneration, tissue erosion and paralysis of the central nervous system and also damages the kidney, liver and pancreas (B.H.Hameed *et al*., 2008). Therefore, it is considered necessary to remove the phenol from industrial effluents before discharging into the water stream.

There are many methods such as adsorption, microbial degradation, chemical oxidation, precipitation, ion exchange and solvent extraction to remove phenols from aqueous solution (M. T. Uddin *et al*., 2007). However, some of those methods are very expensive, use dangerous chemical and generate toxic sludge as by product that harmful to environment and people. Because of that, adsorption process with dried water

hyacinth as adsorbent has been chosen to remove phenol from aqueous solution. This method is economical and safe compare to other adsorbent that very costly and harmful.

Water hyacinth has a huge potential for removal of the vast range of pollutants from wastewater (Maine *et al*., 2001) and that a great number of aquatic systems with water hyacinth as basic component were construct (U.S. EPA *et al*., 1998). Water hyacinths are available, easy to get in our country and the important is it is one of the low cost adsorbent. It can growth in lakes, pond and rivers and proliferate extremely quickly. Dried water hyacinth is chosen because it did not affect the spreading of dengue fever to the residents nearby and easily to handle and keep it. So, water hyacinth are one of the good adsorbents in adsorption of phenol

1.3 Objectives

The objective in this study is to study the removal of phenol from aqueous solution by dried water hyacinth.

1.4 Scopes of Study

There are four scopes of study:

- Effect of initial phenol concentration,
- Effect of dried water hyacinth dosage.
- Effect of pH
- Effect of contact time.

1.5 Rationale And Significance

The purpose of this study is to remove phenol which causes environmental and health problem because it is very harmful even at low concentration and very hazardous chemical because of their potential toxicity to human health. Because of it dangerous physical and chemical properties to biological life including human, flora and fauna, it must be totally remove from the aqueous solution as whether as a habitat, food source or even both. In this study, dried water hyacinth is used as adsorbent because it so plentiful and easy to get in our country.

Water hyacinth tend to grow in large bunches, reproduces rapidly and is considered the weed of the water world. Because of that, it cause major problem in the whole area. Among the problem from water hyacinth is like reduction of fish, physical interferences with fishing, obstruction of shipping routes and losses of water in irrigation systems due to higher evaporation and interference with hydroelectric schemes and increased sedimentation by trapping silt particles and also restricts the possibilities of fishing from the shore with baskets or lines and can cause hygienic problems (Carina C. Gunnarsson *et al*., 2007). By doing this study, the problem can be decrease and improve the environmental problem.

However, dried water hyacinth has many advantages compared to aquatic water hyacinth such as to prevent the dengue fever cause by aquatic water hyacinth and also can cut the cost of the commercialize process. Water hyacinth also one of the low cost and naturally adsorbent that very high efficiency to remove phenol from aqueous solution.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption

2.1.1 Definition and Principles of Adsorption

Adsorption is a process in which atoms or molecules move from a bulk phase which is solid, liquid or gas onto a solid or liquid surface or process by which a liquid or gas adsorbate is adsorbed by an adsorbent. The adsorption media can be operated in liquid or gas phases, in aqueous or solvent phases. Adsorption is to be distinguished from absorption, a process in which atoms or molecules move into the bulk of a porous material, such as the absorption of water by a sponge.

Traditionally, adsorption is classified according to the magnitude of the adsorption forces. Weak interactions (<40 kJ/mol) analogous to those between molecules in liquids give rise to what is called physical adsorption or physisorption. Physisorption is a reversible process where molecule comes in contact with the surface of the media and adheres through mechanical forces. Energy input, such as heat, can cause the molecules to detach from the media surface. Strong interactions (>40 kJ/mol) similar to those found between atoms within a molecule (for example, covalent bonds) give rise to chemical adsorption or chemisorptions. Chemisorption is an irreversible process. Chemisorption is caused by a chemical reaction between the surface of the media and the molecule in the air when it contacts the media surface. To enable the

chemical reaction, specific surface treatments are used depending on the type of molecule to be filtered.

There are several mechanisms which cause the adsorption likes Van der Waals forces, steric interaction, hydrogen bonds, hydrophobicity and polarity. Since the solution to be treated contains a mixture of organics with different properties and the adsorption process is a combination of these mechanisms.

2.1.2 Factor Affecting Adsorption Process

Adsorption is one of the most effective processes of advanced wastewater treatment which industries employ to reduce hazardous organic and inorganic wastes in effluents. It is also used to remove toxic inorganic and organic compound from contaminated ground water (M. Ahmaruzzaman *et al*., 2005).There are many factor that affect efficiency of the adsorption such as:

- *Surface area of adsorbent*. Larger sizes imply a greater adsorption capacity.

- *Particle size of adsorbent*. Smaller particle sizes reduce internal diffusion and mass transfer limitation to the penetration of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly full adsorption capability can be attained). However, wastewater drop across columns packed with powdered material is too high for use of this material in packed beds. Addition of powdered adsorbent must be followed by their removal.

- *Number of carbon atoms*. For substances in the same homologous series a larger number of carbon atoms is generally associated with a lower polarity and hence a greater potential for being adsorbed (e.g., the degree of adsorption increases in the sequence formic-aceticpropionic-butyric acid).

- *Size of the molecule with respect to size of the pores*. Large molecules may be too large to enter small pores. This may reduce adsorption independently of other causes.

- *Degree of ionization of the adsorbate molecule*. More highly ionized molecules are adsorbed to a smaller degree than neutral molecules.

- *pH*. The degree of ionization of a species is affected by the pH (e.g., a weak acid or a weak basis). This, in turn, affects adsorption.

The extent of adsorption also depends on temperature, pressure, and concentration in the bulk phase, elemental nature of the adsorbent. Low temperatures, high pressures, high surface areas, and highly reactive adsorbents generally favor adsorption.

2.2 Adsorbent

Adsorbent is defined as material which has the ability to extract certain substances from gases, liquids, or solids by causing the substances to adhere to its internal surface without changing the adsorbent physically or chemically. The adsorbents are mainly characterized by their surface and porosity either in granular form, powdered form or polymeric adsorbents based on a polystyrene divinyl matrix. There are many adsorbents that can be used to remove contaminants especially phenol from aqueous solution like activated carbon, bentonite, silica gel, activated alumina, water hyacinth and many more. Activated carbon is the most widely used adsorbent and usually prepared from coal, coconut shell, lignite and wood. However, this adsorbent is limited because of its high cost. So, to minimize the cost of water treatment, low cost adsorbent like water hyacinth either living plant or dried should be used to remove contaminants from aqueous solution.

There are many studies have been made by using adsorption process to remove hazardous ions in the water. They use various types of adsorbent which can come from microorganisms as a by-product of fermentation industry, organisms naturally available in large quantities in nature and organisms cultivated or propagated for adsorption purposes using inexpensive media. Table 2.1 below shows some of the studies that have been made by using various types of adsorbent:

Table 2.1: Previous studies with various type of adsorbent

Adsorbent	Species	References
Waste Material (waste of thermal power plants, deoiled soya and agricultural waste)	Coloring agent phenol red	Alok Mittal *et al*.,2009
Water hyacinth	Cadmium and Zinc	S.H Hassan *et al*.,2007
Jackfruit(*Artocarpus heteropyllus*)leaf powder	Methylene Blue	Md Tamez Uddin *et al*.,2009
Hazelnut Shells and Wood Sawdust	Dye	F.Ferrero *et al*.,2007
Palm Ash	Dye	M. Hasnain Isa *et al*.,2007
Water Hyacinth	Azo and Anthraquinone	M.M El Zawahry *et al*.,2004
Phitophora Sp(fresh water algae)	Malachite Green	K. Vasanth Kumar *et al*.,2005
Water Hyacinth	Lead	David Tin Win *et al*.,2003
Water Hyacinth	Cadmium and Zinc	S.H. Hasan *et al*.,2007
Neutralize red mud	Phenol	Ali tor *et al*., 2006
De-oil soya, Agricultural waste material	Malachite Green	Alok Mittal *et al*.,2005

2.3 Water Hyacinth (*Eichhornia crassipens*)

2.3.1 Physical description

Water hyacinth (*Eichhornia crassipes*) is an aquatic plant which can flourish and reproduce floating freely on the surface of water or it can also be anchored in mud (Z. Ismail *et al*., 2009). Nowadays, this tropical plant spread throughout the world and well known as a plant that can double its population in only twelve days and its ability to grow in severe polluted waters. It has shiny light-green, circular leaves that are 2 to 5 inches wide, and attached to inflated stems. The stems have trapped air, and act as an air bladder providing the water hyacinth's buoyancy. Water hyacinth has purple flowers in warm weather. The water hyacinth roots are feathery and a purple-white color. They usually grow from 12 to 18 inches long and they trail down into the water, providing spawning grounds for fish. New plants grow from the mother plant that usually called daughters and the water hyacinth tends to grow in large bunches. Water hyacinth reproduces rapidly and is considered the weed of the water world.

2.3.2 Growth and Habitat

Water hyacinth is an aquatic weed worldwide and grows in lakes, rivers and ponds. It is not winter-hardy and minimum growth temperature is 12^{o} C (54^{o} F).Its optimum growth temperature is 25-30^{o} C (77-86^{o} F) while its maximum growth temperature is 33-35^{o} C (92-95^{o} F). Water hyacinths regenerate prolifically from fragments of stems and the seed can remain viable for more than six years. The plant normally forms cohesive floating mats and can cover large areas of the water surface. The spreading of the water hyacinth is also thought to be enhanced by winds. The plant flourishes in nutrient-rich waters and on shallow shores with mud rich in nutrients.

2.3.3 Characteristic of Water Hyacinth

The water hyacinth has an excellent ability to take up nutrients and other chemicals from its environment, and the chemical composition of the water hyacinths depends strongly on its environment. The nutrient content is lower in the stem and root compared with the nutrient content in the leaves.

Most of the common pollutants in water are positive ions. One possible theory of a way to remove them would be to put a negatively charged object into the water and use it to attract the positively charged ions. This is essentially what we are doing when we put the roots of a water hyacinth plant into the polluted water. The roots of many plants including water hyacinth have a negative charge to them. When you put this negative charge into the water it acts as a magnet to the positively charged ions. The theory would be that the roots still have a negative charge to them after the plant has died and that this charge would still be strong enough to attract the positive ions of a heavy metal.

2.3.4 Environmental Problem of Water Hyacinth and How to Control

Water hyacinth is listed as one of the most productive plants on earth and is considered one of the world's worst aquatic plants. The rapid growth rate of invasive species, *Eichhornia Crassipes*, has caused problems in lakes and river throughout the world (Wenbing Zhout *et al*., 2009).

Lately, the hyacinth has invaded many tropical lakes including Lake Victoria, East Africa where it caused several problems. Water hyacinths can double its size in 5 days and a mat of medium sized plants may contain 2 million plants per hectare that weigh 270 to 400 Tonnes. These dense mats interfere with navigation, recreation, irrigation, and power generation. The blockage of canals and rivers by water hyacinth can cause dangerous flooding and serious implications where water is already scarce. Water hyacinth can also present many problems for the fisherman such as decreased fish

population, difficult access to the fishing sites and loss of fishing equipment, resulting in reduction in catch and subsequent loss of livelihood. The rapid growth of water hyacinth also can hinder the growth of any other plants growing in the aquatic environment. This causes an imbalance in the aquatic ecosystem and often means that a range of fauna that relies on a diversity of plant life for its existence can become extinct. The dense mat water hyacinth form blocks light penetration for submerged or other smaller floating plants that might be present in the water. On the other hands, Water hyacinth has been a major environmental concern in tropical developing countries. It has been a micro habitat for several diseases causing vectors carrying malaria, bilharziosis and river blindness to proliferate. The diseases associated with the presence of aquatic weeds in tropical developing countries are among those that cause the major public health problems such as malaria, schistosomiasis and lymphatic filariasis.

Water hyacinth has apparently become a problem in different parts of the world due to its uncontrolled and rapid growth. Therefore, there is a need to manage its spread through suitable control measures. Tables 2.2 below show the method to control water hyacinth:

Table 2.2: Methods for control of water hyacinth (Anushree Malik *et al*., 2007)

Control Methods	**Agents**	**Limitation**
Physicals	Permanent drainage of area	Not always feasible
	Manual removal by hand pulling or harvesting nets	Difficult and labor intensive, may involve health risk
	Mechanized removal through land-based cranes, draglines or, by water-based machinery such as mowers, dredges, barges or aquatic weed harvesters	Expensive, energy intensive, need a convoy of water and land-based vehicles for transportation of harvested mats

Control Methods	**Agents**	**Limitation**
Chemicals	2,4-dichlorophenoxyacetic acid (2,4-D) + complexed copper 2,4-D amine spray at 2l/ha followed by 2nd spray at 1 l/ha Endothall dipotassium salt, endothall dimethylalkylamine salts, glyphostate	Expensive, cannot control large infestations, long term adverse effects on other communities and environment
Biological	Classical control by insects: Neochetinaeichhorniae, N. bruchi and Sameodes albiguttalis Allelopathic plants Coleus amboinicus leaf powder (40 g/l) Lantana Partheniu Cassytha powder Fungal pathogens such as Alternaria eichhorniae	Insufficient reduction and resurgence in growth Still under R&D stage, may not suffice alone and better if used with mechanical/chemical control methods

2.4 Phenol

2.4.1 General Description and Applications

Phenol is the simplest aromatic alcohol which characterized by a hydroxyl (-OH) group attached to a benzene ring with the chemical formula C_6H_5OH.The term phenol is not only for phenol itself but also for a class of aromatic compounds possessing a hydroxyl group attached to a benzene ring or a complex ring system. Phenol in water solution is sometimes called **carbolic acid**. Phenols differ from aliphatic alcohols which hydroxyl group is bonded to a saturated carbon atom. Due to the tendency of pi-orbital overlap between carbon and oxygen, phenol can lose easily the H^+ ion from the hydroxyl group, resulting in higher acidity than aliphatic alcohols (but weaker acidity than carboxylic acids). The intermediate state losing hydrogen ion (H^+) from the hydroxyl group in a phenol is called phenolate anion $C_6H_5O^-$. It reacts with strong bases to form salts called phenolates.

Pure phenol is a white crystalline solid. It is moderately soluble in water and is soluble in ethanol and ether. Phenols form stronger hydrogen bonds than aliphatic alcohols and. Phenols are more soluble in water than alcohols and have higher boiling points. Many phenols have a sharp, spicy odor, but phenol smells bland and sweetish. Presence of phenol in water supplies is noticed as bad taste and odor (S.Rengaraj *et al*., 2002). It is highly toxic and caustic. Some phenols interfere with the endocrine system and disrupt the function of hormones. They have antiseptic property and are used in formulating disinfectants, deodorizers, and pesticides.

Phenol is synthesized by either the hydrolysis of chlorobenzene (Raschig process) or the oxidation of cumene in air to form cumene hydroperoxide which is then cleaved into phenol and acetone, a valuable by-product (Cumene process). Phenols are acidic and react with strong bases to form alkali-metal salts known as phenoxides. The most important reaction of phenol is its condensation (which produces water as a side effect) with formaldehyde.

Phenol can be highly toxic even at low concentration and their concentrations in media are strictly limited by regulations. In recent years, several physico-chemical treatments have been proposed for obtaining efficient phenol removal such as adsorption, air stripping, steam stripping, wet oxidation, heterogeneous photocatalysis and biological treatment (I. Vazquez *et al*, 2007)

Phenol is used primarily as an intermediate in the production of phenolic resins. It is used in the manufacture of nylon, polycarbonate and epoxy resins. Phenol also is used in slimicides (chemicals that kill bacteria and fungi in slimes), as a disinfectant, antiseptic and in medicinal preparations such as mouthwash and sore throat lozenges. Phenol is also used in the preparation of cosmetics including sunscreens, hair dyes, and skin lightening preparations. In cosmetic surgery, phenol serves as an exfoliant. It is also used in phenolization, a surgical procedure used to treat an ingrown nail, in which it is applied to the nail bed to prevent regrowth of nails. 5% Phenol is sometimes injected near a sensory nerve in order to temporarily (up to a year) stop it from transmitting impulses in some intractable cases of chronic neuropathic pain.

2.4.2 Physical and Chemical Properties

Phenol exists naturally and is manufactured in large quantity (about 7 billion kg/year) as a precursor to many materials and useful compounds. It is found in nature in some foods, in human and animal wastes and in decomposing organic material. Phenol is produced by the body and excreted independent of external exposure or intake. The normal range of phenol in the urine of unexposed individuals is 0.5 to 80 milligrams of phenol per liter of urine. Table 2.3 shows the physical and chemical properties of phenol: