Removal of Phenol from Industrial Wastewaters Using Lignitic Coals

By

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ABSTRACT

Phenol adsorption capacity of lignitic coals which were obtained from Soma and Yatağan / Turkey was investigated under different operational conditions such as solid – liquid ratio (S/L), reaction time, initial phenol concentration and temperature. Based on batch adsorption studies, it was observed that the phenol was completely adsorbed by coal depending on time of adsorption and the S/L ratio. From these results, the maximum adsorption values on the time axis at various S/L ratios were used and the fractions of phenol receptive adsorption sites on coal surfaces were calculated as 60 % and 43 % for Soma and Yatağan coals, respectively.

Freundlich adsorption isotherm was found to describe the adsorption of phenol on lignitic coals well. The Langmuir model did not describe the system as good as Freundlich model most probably due to the monolayer coverage assumption on this model.

Activation energy and the maximum heat of adsorption calculated using adsorption data at different temperatures by the Arrhenious and Van't Hoff equations were 10.3 and -20.2 kJ/mol, respectively. The low energies suggest that the adsorption of phenol on these lignitic coals were through physical interactions. An adsorption mechanism of phenol on lignite was discussed based on these findings.

Residual water quality following adsorption in terms of major elements and heavy metals was within acceptable limits defined for wastewaters. The amount of organic matters dissolved from coals were also negligable.

The presence of heavy metals as Cu, Zn etc. in water as a contaminant was also found to affect the removal of phenol by about 10-20 %.

ÖZ

Soma ve Yatağan / Türkiye ‘den elde edilen linyit kömürlerinin fenol adsorblama kapasitesi, katı-sıvı oranı, reaksiyon süresi, başlangıç fenol konsantrasyonu ve sıcaklık gibi farklı koşullar altında araştırılmıştır. Yapılan kesikli deney çalışmalarına dayanılarak, fenolün, kömür tarafından, adsorpsiyon süresi ve katı-svı oranına bağlı olarak tamamen adsorblandığı görülmüştür. Bu sonuçlardan, zaman eksenindeki ve değişik katı–sıvı oranlarındaki maksimum adsorbsiyon değerleri kullanılmış ve kömür yüzeylerinin fenol alıcı adsorbsiyon kısımları oranları, sırasıyla, Soma ve Yatağan kömürleri için % 60 ve % 43 olarak hesaplanmıştır.

Freundlich adsorbsiyon izoterminin, linyit kömürü üzerine fenol adsorbsiyonu sistemini iyi temsil ettiği bulunmuştur. Langmuir model, büyük ihtimalle tek tabaka varsayımına dayandığı için, sistemi Freundlich modeli kadar iyi temsil etmemiştir.

Aktivasyon enerjisi ve maksimum adsorbsiyon ısısı, değişik sıcaklıklarda, Arrhenious ve Van’t Hoff denklemleri kullanılarak, sırasıyla, 10.3 ve -20.2 kJ/mol olarak hesaplanmıştır. Düşük enerji değerleri, bu linyit kömürleri üzerine fenol adsorbsiyonunun fiziksel etkileşim ile olduğunu işaret etmiştir. Bu bulgulara dayanarak, linyit üzerine fenol adsorbsiyonu mekanizması tartışılmıştır.

Temel elementler ve ağır metaller açısından, adsorbsiyonu takip eden atıksu kalitesi, atıksular için belirlenmiş kabul edilir limitler arasındadır. Kömürden çözünen organik maddeler de ihmal edilebilir derecededir.

Ağır metallerin (Cu, Zn vs.), bir bileşen olarak suda bulunmasının, aynı zamanda fenol uzaklaştırılmasını %10-20 oranında etkilediği bulunmuştur.

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CHAPTER I

INTRODUCTION

1.1. Statement of the Pollution Problem

Since World War II, depending on the increase of the world population and development of the industrial applications, environmental pollution and other environmental problems became important. There has been a huge growth in the manufacture and uses of synthetic chemicals since the beginning of the 20th century. There still are many possible sources of chemical contamination. These include wastes from industrial chemicals production, metal plating operations, and pesticide run off from agricultural lands, and the other industrial applications and productions. (Monahan S., 1998)

The number of organic compounds that have been synthesised since the turn of the century now exceeds half a million, and 10.000 new compounds are added each year. As a result, many of these compounds are now found in the wastewaters from most municipalities and communities. Currently, the release of volatile organic compounds (VOCs), non-volatile or semi-volatile organic compounds and volatile toxic organic compounds (VTOC) found in wastewater is of great concern in the operation of both collection systems and treatment plants.

All Industries use specific chemicals or the other raw materials to produce their last products. Production has long steps which is the total of many reactions. So, each process can produce hazardous wastes. A waste is considered a hazardous if it is reactive, ignitable, corrosive or toxic. Ninety five chemicals have been defined as toxic including phenol on the basis of production volume, exposure, and biological effects. (Kent J. A.,1992).

Organic compounds in water derive from the natural decomposition of plant and animal material from industrial, urban, or agricultural pollutants and from the reaction of halides (most often chlorine) with natural organics during water treatment. Concentrations range from none in protected ground waters to 10-30 mg/L in naturally productive or contaminated surface water (Montgomery J.M., 1985).

Hydrocarbons in these wastewaters are in many forms such as chlorinated hydrocarbons, halogenated hydrocarbons, organophosphates and non volatile or semi volatile aromatic hydrocarbons. Phenol, as an aromatic semi volatile hydrocarbon, presents in wastewaters of most industries such as high temperature coal conversion, petroleum refining, resin and plastic, leather and textile manufacturing (Rengaraj S. *et al.* 2001), oil refineries, chemical plants, coke ovens, aircraft maintenance, foundry operations, paper-processing plants, paint manufacturing, rubber reclamation plants, nitrogen works, and fiberglass manufacturing in different ranges from 1 mg/L to 7000 mg/L. (Table 1.1). Phenolic constitutes are 11th of the 126 chemicals which have been pointed as priority pollutants according to United States Environmental Protection Agency (EPA, 2002).

Table 1.1. Levels of Phenol Reported in Industrial Wastewaters (Metcalf and Eddy, 2003)

Industrial Source	**Phenol Concentration (mg/L)**
Petroleum refineries	40 - 185
Petrochemical	200 - 1220
Textile	100 - 150
Leather	4.4 - 5.5
Coke ovens (without dephenolization)	600 - 3900
Coal conversion	1700 - 7000
Ferrous industry	5.6 - 9.1
Rubber industry	3 - 10
Pulp and paper industry	22
Wood preserving industry	50 - 953
Phenolic resin production	1600
Phenolic resin	1270 - 1345
Fiberglass manufacturing	40 - 2564
Paint manufacturing	1.1

İzmir and Aegean Region act a major role in Turkey's Industry producing different industrial products. The industries that produces phenol contaminated wastewater in İzmir and Aegean Region were listed in Table 1.2.

Table1.2. Content of Industrial Wastewater from İzmir Region (DIE & EBSO, 2002)

Sector	**Establishment**		**Aromatic Hydrocarbon Pollutant**
	total	**%**	
Textile	338	32.4	**Phenol,** 2,4,6 trichlorophenol, pentachlorophenol, benzene,1,1 dichloroethylene, 1,1 dichloroethane, chloroform, 1,1,1 trichloroethane, trichloroasetilene, tetrachloroethylene, vinylchloride, toluene, ethylbenzen.
Food	158	15.2	**Phenol** and phenolic compounds
Leather	51	4.9	**Phenol,** 2,4,6 trichlorophenol, pentachlorophenol, 1,1 dichloroethylene, chloroform, 1,1,1 trichloroethane, trichloroasetilene, tetrachloroethylene, benzene, toluene, ethylbenzene
Coal and petroleum	41	3.9	**Phenol**, benzene, toluene
Tobacco	16	1.5	**Phenol** and phenolic compounds
Wood	17	1.6	2,4,6 trichlorophenol, pentachlorophenol, 1,1,1 trichloroethane, benzene, toluene, ethylbenzene
Paper	21	2.0	**Phenol,** 2,4,6 trichlorophenol, pentachlorophenol, Chloroform, 1,1,1 trichloroethane,
Printing	22	2.1	**Phenol,** pentachlorophenol, 1,1 dichloroethylene, 1,1 dichloroethane, chloroform, 1,1,1 trichloroethane, trichloroasetilene, tetrachloroethylene, benzene, toluene, ethylbenzene
Plastic	64	6.1	**Phenol,** ethylbenzene, 1,2 dichloroethane,toluene
Non-metal industry	53	5.1	Ethylbenzene, pentachlorophenol, toluene, benzene 1,2 dichloroethylene, 1,1 dichloroethane, chloroform, 1,1,1 trichloroethane, hexachloroethane, trichloroasetilene.

Table1.2. Content of Industrial Wastewater from İzmir Region (continue)

Sector	**Establishment**		**Aromatic Hydrocarbon Pollutant**
	total	**%**	
Metal industry	41	3.9	**Phenol,** 2,4,6 trichlorophenol, pentachlorophenol, 1,1 dichloroethylene, 1,1 dichloroethane, 1,1,1 trichloroethane, trichloroasetilene, tetrachloroethylene,, benzene, toluene, ethylbenzene.
Nonferrous industry	85	8.2	Ethylbenzene, pentachlorophenol, toluene, benzene 1,2 dichloroethylene, 1,1 dichloroethane, chloroform, 1,1,1 trichloroethane, hexachloroethane, trichloroasetilene
Electricity	30	2.9	1,2 dichloroethylene, chloroform, trichloroasetilene, tetrachloroethylene, 1,1,1 trichloroethane, 1,2 dichloroethane
Medical	19	1.8	Pentachlorophenol, 1,1 dichloroethylene, 1,1,1 trichloroasetilene tetrachloroethylene, benzene, toluene, 1,2 dichloroethane
Motor transportation	34	3.3	**Phenol,** 2,4,6 trichlorophenol, pentachlorophenol, benzene, 1,1 dichloroethylene, 1,1 dichloroethane, chloroform, 1,1,1 trichloroethane, trichloroasetilene, tetrachloroethylene, vinyl chloride, toluene, ethylbenzene
Motor vehicles	13	1.2	**Phenol,** pentachlorophenol, benzene, toluene, chloroform, *trans* 1,2 dichloroethylene, 1,2 dichloroethane 1,1,1 trichloroethane, trichloroasetilene, tetrachloroethylene, ethylbenzene
Furniture	39	3.7	**Phenol,** Pentachlorophenol, 2,4,6 trichlorophenol, chloroform, 1,1,1 trichloroethane, benzene, toluene, ethyl benzene.
Total	**1042**	**100**	

It is seen from the Table 1.2. that, establishment of textile, leather and petrochemical manufacturing is more than 40 % of the whole industry in İzmir. All these sectors produce wastewaters which contain phenol and phenolic compounds. There are 2174 firms which act textile area in Turkey and 338 of these firms are in İzmir (15.5 %). In leather manufacturing, there are 129 big firms in Turkey and 13 of these in İzmir (10 %). Both these two industrial sectors use huge amounts of water in their different process, and finally discharge huge amounts of wastewater contain organic pollutants. Coal and Petroleum Refining processes are also a cause of phenol pollution in İzmir and its environment.

In order to make clear the importance of pollution which is caused by textile and leather manufacturing in İzmir, the main characteristic properties of these kinds of wastewaters are listed in Table 1.3 and Table 1.4. Textile wastewaters contain approximately seven times much more phenol than its maximum allowable value. Chemical Oxygen Demand (COD) of leather wastewaters can be reached to limits of 5000 mg/L and it is known that effect of phenol on COD value is very important. All these wastewaters need cost effective treatment processes.

Table 1.3. Characterization of Textile Wastewaters in İzmir.

POLLUTANT	**Pollutant Ranges* (mg/L)**	**Maximum Allowable Value** (mg/L)**
Phenols	2.02-3.2	0.5
Sulphur (S)	2.30-3.8	0.1
Cyanide (CN)	0.03-0.07	-
Lead (Pb)	0.24	-
Chromium (Cr)	0.04-0.42	1.0
Cadmium (Cd)	0.03-0.07	-
Copper (Cu)	0.05-0.82	-
Nickel (Ni)	0.31	-
Ferrous (Fe)	0.95	-
Zinc (Zn)	0.05-2.40	10

* *Environmental Problems in İzmir, (2000)*

** *Regulations of Water Quality Standards in Turkey*

Table 1.4. Characterization of Leather Wastewaters in İzmir.

POLLUTANT	Pollutant Ranges** (mg/L)	Maximum Allowable Value*** (mg/L)
pH	7.41-8.10	6-9
COD* (mg/L)	52-4810	200
Chromium (mg/L)	1.7-15.2	0.3
Sulphur (mg/L)	2.4-120	1.0
Oil and gress (mg/L)	0.04-0.42	20

**COD is related to organic pollution including phenol*

*** Environmental Problems in İzmir, 2000*

****Regulations of Water Quality Standards in Turkey*

1.2. Health Effects

Phenol has acute and chronic effects on human health. Inhalation and dermal exposure to phenol is highly irritating to skin, eyes, and mucous. These invers effects also known as acute (less than 14 days-exposure) effects of phenol. The other acute health effects are headache, dizziness, fatigue, fainting, weakness, nausea, vomiting and lack of appetite at high levels. Effects from chronic exposure (longer than 365 days) include irritation of the gastrointestinal tract. Phenol also can change blood pressure and can cause liver and kidney damage. Nervous system is affected negatively for long time exposures (EPA, 2002). EPA (Environmental Protection Agency) has classified phenol as a Group D, not classifiable as to human carcinogenicity. Animal studies have not shown tumors resulting from oral exposure to phenol, while dermal studies have reported that phenol applied to the skin may be a tumor promotor and/or a weak skin carcinogen in mice.

1.3. Methods Used to Remove Phenols from Industrial Wastewaters.

Wastewaters are usually classified as industrial wastewater or municipal wastewater. Industrial wastewater with characteristics compatible with municipal wastewater is often discharged to the municipal sewers. Characteristics of industrial wastewaters vary greatly from industry to industry, and consequently, treatment process for industrial wastewater also vary.

Current treatment technologies are available to remove phenol from wastewaters. Both physicochemical and biological treatment techniques are successful in full scale industrial use, and high efficiencies of phenol removal can be obtained. Phenolic wastes also contain other contaminants which require additional special treatment procedures. For example, in case of wastewaters from petroleum industry, organic pollutants are removed by biological treatment or chemical oxidation methods (Metcalf and Eddy, 2003). In addition to biological treatment and chemical oxidation methods, another method for phenol removal is also used such as adsorption on to granular activated carbon (Thong Z. *et. al,* 1998). Choice of a suitable and effective treatment technique depends on economic factors and special wastewater characteristics. The commonly used treatment methods will be discussed in the following paragraphs.

1.3.1. Adsorption onto Granular Activated Carbon

The most common method for the removal of dissolved organic material is adsorption on activated carbon, a product that is produced from a variety of carbonaceous materials, including wood, pulp-mill char, peat, and lignite. Effectiveness of these materials come from its tremendous surface area. The carbon is produced by charring the raw material anaerobically below 600 ^{0}C followed by an activation step consisting of partial oxidation. Carbon dioxide may be employed as an oxidizing agent at 600-700 ^{0}C, or the carbon may be oxidized by water at 800-900 ^{0}C . These oxidation processes are given below.

$$CO_2 + C \longrightarrow 2CO$$

$$H_2O + C \longrightarrow H_2O + CO$$

These processes develop porosity, increase the surface area, and leave the C atoms in arrangements that have affinities for organic compounds.

Activated carbon might be in two general types: granulated activated carbon, consisting of particles 0.1 – 1 mm in diameter, and powdered activated carbon, in which most of the particles are 50-100 μm in diameter. For water treatment, currently granular carbon is more widely used. It may be employed in a fixed bad, through which water flows downward. Accumulation of particulate matter requires periodic backwashing.

Economics require regeneration of the carbon, which is accomplished by heating it to 950 ^{0}C in a steam air atmosphere. This process oxidizes adsorbed organics and regenerates the carbon surface, with an approximately 10% loss of carbon. (Monahan S., 1998)

1.3.2. Solvent Extraction

Solvent extraction is also called liquid extraction and liquid-liquid extraction. Solvent extraction occurs when a waste constituent in the wastewater is selectively removed when it is contacted with an organic solvent, because it is more soluble in the solvent than it is in the wastewater. Solvent extraction method is predominantly applied for organic material separation from wastewaters. In this process, the solvent and the waste stream are mixed to allow mass transfer of the contaminant from the waste to the solvent. The solvent, immissible in water, is then allowed to separate from the water by gravity. The solvent solution containing extracted contaminant is called the extract. The extracted waste stream with the contaminants removed is called the raffinate. If the extract is sufficiently enriched, it may be possible to recover useful material. For the recovery of the solvent and reusable organic chemical from organic material, distillation is often employed. The solvent extraction process has found wide application in the ore processing industry, in food processing, and in the petroleum industry (Davis. L. *et al,* 1991).

1.3.3. Chemical Oxidation

Chemical oxidation by both ozone and chlorine has been reported effective for some toxic organics including phenol. It is possible to reach 48 % removal efficiency for phenol at pH 7 and initial phenol concentration of 1000 mg/L using ozone as an oxidant reagent. Several factors influence the effectiveness of the oxidation process, such as reactivity of the ozone itself with the target compound, the rate of reactivity, the ozone demand to achieve a desired degree of treatment, the extent of incidental stripping associated with ozone dispersion, and other treatment variables such as pH and temperature. For example, in ozone treatment of phenol, treatment proceeds at pH 11 at a rate approximately twice as fast as at pH 7 (Metcalf and Eddy, 2003).

1.3.4. Biological Treatment Process

Phenolic compounds, especially chlorinated ones, are similar to herbicides and pesticides in structure and they are difficult to remove by biological treatment processes because of their resistance of biodegradation. (Rengaraj S. *et al*, 2001). However Phenol can be removed from wastewater by different treatment method including biochemical ways. (Galiatsatou P. *et al,* 2002)

Biological treatment involves the action of living microorganisms. The various microorganisms utilize the waste material as food and convert it into simpler substances by natural metabolic process. Organic waste from the petroleum industry can be treated biologically. In addition to the traditional biological treatment systems (activated sludge and trickling filter processes), a treatment method called land farming and land treatment may be used. The waste is carefully applied to and mixed with surface soil, microorganisms and nutrients may also be added to the mixture, as needed. The toxic organic material is degraded biologically, whereas inorganic materials are adsorbed in the soil (Nathanson, A.J, 1997). Phenol concentrations up to 500 mg/L are generally considered suitable for biological treatment techniques. (Metcalf and Eddy, 2003)

Certain organic hazardous wastes can be treated in slurry from in an open lagoon or in a closed vessel called a bioreactor. A bioreactor has fine bubble diffusers to provide oxygen and mixing device to keep the slurry solids in suspension. (Nathanson A.J., 1997)

1.4. The Scope of the study

The scope of this study was to investigate the removal of phenol from aqueous systems (simulated wastewater) by natural lignitic coals which were obtained from Soma and Yatağan Power Plants. There is a growing interest in the preparation of low cost adsorbents for wastewater plants, so usage of natural (untreated) and abundant materials are important for the cost-cutting of the processes.

Batch adsorption experiments were carried out under various operational conditions such as solid/liquid ratio, reaction time, temperature, and phenol concentration to study followings:

- Phenol adsorption capacity of coal
- Phenol adsorption mechanism on coal.
- Residual water quality after adsorption.
- Effects of heavy metals on phenol adsorption.

CHAPTER II

PHENOL AND ITS ADSORPTION ON DIFFERENT SUBSTRATES

Hydrocarbons are compounds that contain only carbon and hydrogen, and divided into two main classes, aliphatic hydrocarbons and aromatic hydrocarbons. This classification dates from the nineteenth century, when organic chemistry was almost exclusively devoted to the study of the materials from natural sources and terms were coined that reflected the origin of a substance. Two such sources were fats and oils, and the word *aliphatic* was derived from the Greek word *aleipar* ("fat") for these materials. Aromatic hydrocarbons, irrespective of their own odour, were typically obtained by chemical treatment of pleasant – smelling plant extracts. (Loudon, G.M., 1995)

It is also possible to classify hydrocarbons according to their carbon bonds. These are **saturated hydrocarbons** (alkanes) in which all carbon-carbon bonds are single bonds, and **unsaturated hydrocarbons** in which the molecules have at least one carbon-carbon double bond (alkenes) or triple bond (alkynes). Aromatic compounds, originally named for their aromas, also fall into the unsaturated designation (Philip, S., 1999). Another name for aromatic hydrocarbons is arene. Arenes have properties that are much different from alkanes, alkenes and alkynes. The most important aromatic hydrocarbons are benzene and its monohydoxy derivative of phenol. (Loudon, G.M., 1995)

Hydrocarbons such as alkanes are water insoluble. This is because water is a polar solvent (Polar O – H bonds) and alkanes are non polar (composed of non polar carbon-carbon and carbon hydrogen bonds). Hydrocarbons are also less dense than water and float on its surface (oil spills remain on the ocean's surface, for example) (Philip, S., 1999).

Organic compounds that have a boiling point of lower than 100 °C and/or a vapor pressure of higher than 1 mm-Hg at 25 °C are generally considered to be volatile organic compounds (VOCs). For example vinyl chloride, which has a boiling point of -13.9 °C and a vapor pressure of 2548 mm Hg at 20 °C is an example of extremely VOC. Volatile organic compounds can be removed from wastewaters by air-stripping method. (Kent J.A., 1992)

Phenol has a boiling point of 182 °C which is higher than 100 °C, and a vapor pressure lower than 1 mm Hg (0.41 mm Hg at 25 °C). Therefore, phenol is out of the volatility range and can not be removed by air-stripping method.

2.1. Structure of Phenol

The monohydroxy derivative of benzene is known as phenol. (Sawyer N.C. *et. al,* 1994). Phenol is recovered from coal tar, and considerable amounts are manufactured synthetically. It is a colourless or white solid when it is pure; however, it is usually sold and used as a liquid. It has the chemical formula as C_6H_6O and the molecular weight of 94,144 g /mol. The odour threshold for phenol is 0.04 ppm, with a strong very sweet odour reported. It is very soluble in water and quite flammable. The vapour pressure for phenol is 0,41 mm Hg at 25 ^{0}C, and it has a log octanol / water partition coefficient (Log K_{OW}) of 1,46. Chemical structure of phenol is illutrated in Figure 2.1., and physical properties are given in Table 2.1.

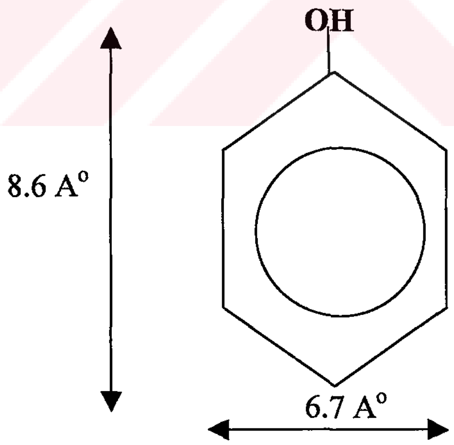

Figure 2.1. Structure and dimensions of phenol (Koltuksuz G., 2002).

Table 2.1.The Main Physical Properties of Phenol

Properties	**Values**
Molecular weight (g/mol)	94.144
Molar volume (cm^3/mol)	90
Boiling point (°C)	182
Melting point (°C)	43
Auto ignitition temperature (°C)	715
Solubility in water (mg/L)	50-100 @ 19 °C
Liquid density (g/cm^3)	1.06
pH of aqueous solution	6
Molecular diffusivity in water (cm/sec)	6.0 x 10^{-4}
Vapour pressure (mm Hg)	0.41 @ 25 °C
Relative vapour density	3.24 (air=1)
Air-water partition coefficient, K_{aw}(25 °C)	2.5 x 10^{-5}
Dipole moment (debyes)	1.450007
Polarizability, Π_i	0.89
Liquid surface tension (dynes/cm)	36.5 @ 55 °C
Excess free energy (kJ/mol)	10
Excess enthalpy (kJ/mol) [S/D]*	1/8
Excess entropy (J/mol K) [S/D]*	-9/-2
Acidity constant, pKa(25 °C)	9.90
Fraction in neutral form at pH 7	0.998

[S/D]* *saturated/dilute solution*

Phenol is used in making plywood, construction, automotive and appliance industry as a raw chemical and in the production of nylon, epoxy resins. In addition, it becomes a disinfectant, slime-killing agent, and an additive in medicines. Production of biphenol A is another usage area of phenol. (Metcalf and Eddy, 2003).

2.2. Adsorption Process and Phenol Adsorption on Different Substances

2.2.1. Adsorption Process

Adsorption is the physical and/or chemical process in which a substance is accumulated at an interface between phases. For the purposes of water or wastewater treatment, adsorption from solution occurs when impurities in the water accumulate at a solid-liquid interface. The substance which is being removed from the liquid phase to the interface is called as adsorbate, and solid phase in the process is known to be adsorbent. (Montgomery J.M., 1985)

Dissolved species may participate directly in air-water exchange while sorbed species may settle with solids. Figure 2.2. illustrate a brief adsorption process for a general aromatic organic matter.

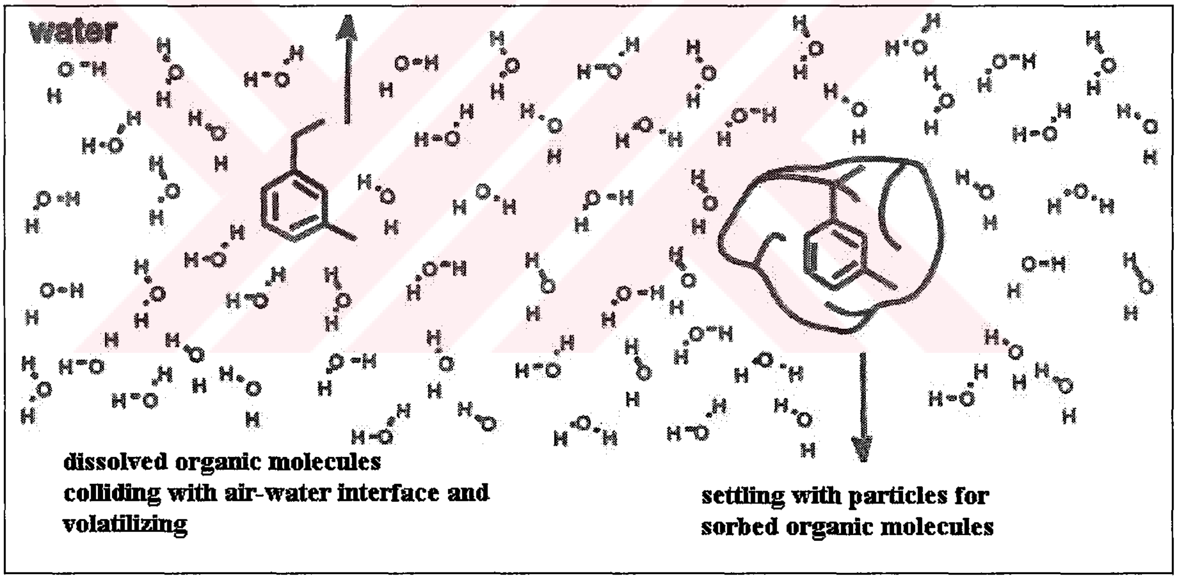

Figure 2.2. Illustration of sorbed species behave differently from dissolved molecules of the same substance (Schwarzenbach R.P., 2003).

Physical adsorption (physisorption) is relatively non-spesific and is due to the operation of weak forces between molecules. In this process, the adsorbed molecule is not affixed to a particular site on the solid surface, it is free to move over the surface (Sawyer N.C. *et. al,* 1994). The physical interactions among molecules, based on electrostatic forces, include dipole-dipole interactions, dispersion interactions and hydrogen bonding. When there is a net seperation of positive and negative charges within a molecule, it is said to have a dipole moment. Molecules such as H_2O and N_2 have permanent dipoles because of the configuration of atoms and electrons within them. Hydrogen bonding is a special case of dipole-dipole interaction and hydrogen atom in a molecule has a partial positive charge. Positevely charged hydrogen atom attracts an atom on another molecule which has a partial negative charge. When two neutral molecules which have no permanent dipoles approach each other, a weak polarization is induced because of interactions between the molecules, known as the dispersion interaction. (Montgomery J.M., 1985) Figure 2.3. illustrates the main interactions and forces during physical adsorption processes.

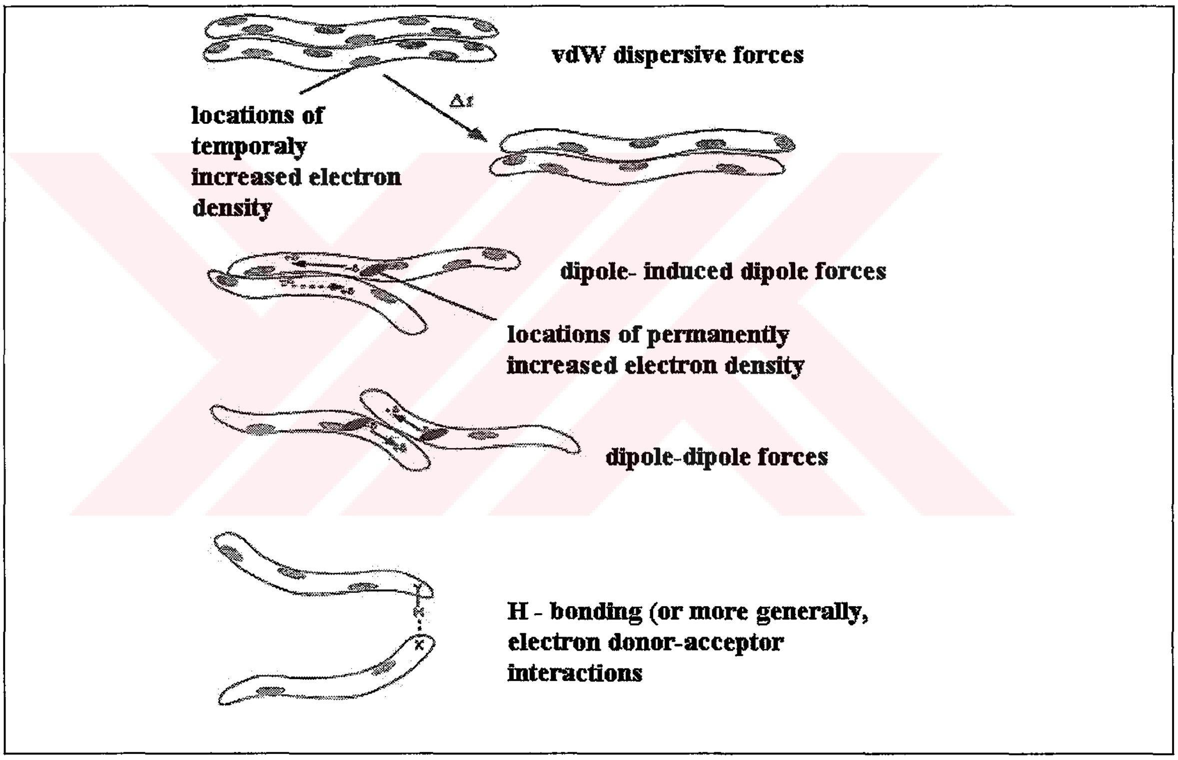

Figure 2.3. Illustration of the various molecular interactions arising from uneven electron distributions (Schwarzenbach R.P., 2003).

In water treatment, adsorption of an organic adsorbate from polar solvent (water) onto a nonpolar adsorbent (carboneous material) has an often interest. In general, attraction between adsorbate and polar solvent is weaker for adsorbates of a less polar nature; a nonpolar adsorbate is less stabilized by dipole-dipole or hydrogen bonding to water. Nonpolar compounds are adsorbed more strongly to nonpolar adsorbents. This is known as hydrophobic bonding. Hydrophobic compounds adsorb on to carbon more strongly. Longer hydrocarbon chain is more nonpolar, so, degree of this type of adsorption increases with increasing molecular length. (Montgomery J.M., 1985)

Additionally, branched chains are usually more adsorbable than straight chains, an increasing length of the chain decreases solubility. An increasing solubility of the solute in the liquid decreases its adsorbability. For example, hydroxyl groups generally reduces adsorption efficiency. Carboxyl groups have variable effects according to the host molecule. Double bonds affect adsorbability of organic compounds depending on the carboxyl groups. The other effective factor on adsorption is molecular size. (Eckenfelder W.W., 2000) aromatic and substituted aromatic compounds are more adsorbable than aliphatic hydrocarbons (Metcalf and Eddy, 2003). Figure 2.4. illustrates the adsorption of an aromatic compound on to a polar surface.

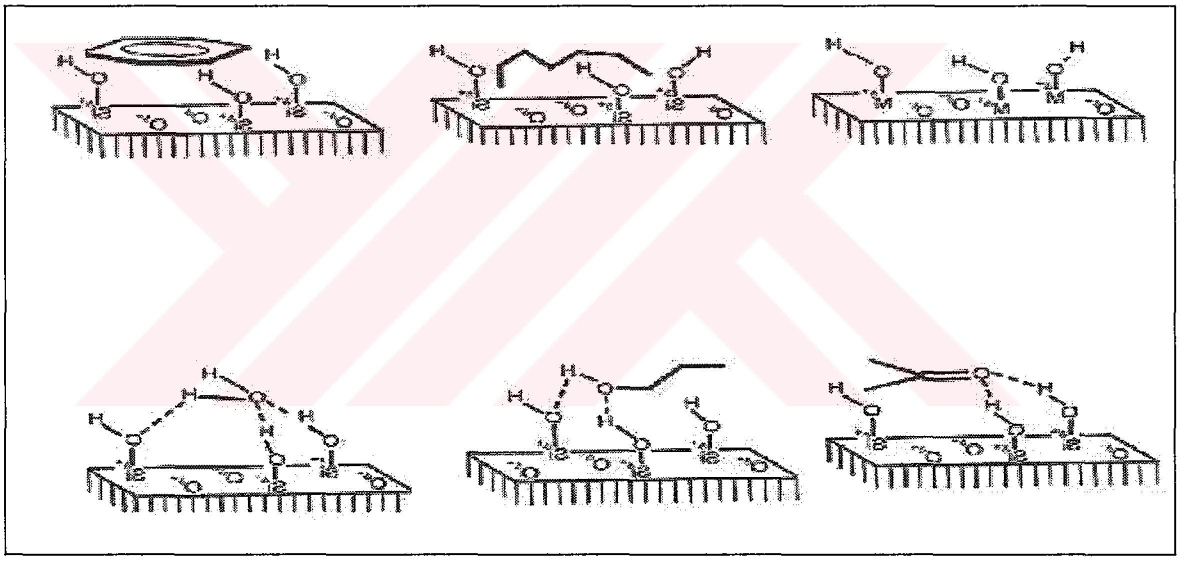

Figure 2.4. Illustration of the aromatic hydrocarbon sorption on a polar inorganic surface (Schwarzenbach R.P., 2003).

Chemical adsorption, (chemisorption) is also based on electrostatic forces, but much stronger forces act a major rols on this process. (Sawyer N.C. *et.al,* 1994). In chemisorption, the attraction between adsorbent and adsorbate is a covalent or electrostatic chemical bond between atoms, with shorter bond length and higher bond energy (Montgomery J.M., 1985).

The enthalpy of chemisorption is very much greater than that for physisorption, and typical values are in the region of 200 kJ/mol, whereas this value for physisorption is about 20 kJ/mol. Except in special cases, chemisorption must be exothermic. A spontaneous process requires a negative free energy (ΔG) value. Because, the translational freedom of the adsorbate is reduced when it is adsorbed, entropy (ΔS) is negative. Therefore, in order for $\Delta G = \Delta H - T\Delta S$ to be negative, ΔH must be negative, and the process exothermic. If the enthalpy values less negative than -25 kJ/mol, system is physisorption and if the values more negative than -40 kJ/mol it is signified as chemisorption (Atkins P.V., 1994).

Table 2.2. The Bond Energies of Various Mechanisms for Adsorption. (Atkins P.V., 1994)

Interaction between adsorbent and adsorbate	**Enthalpy (kJ/mol)** **$-\Delta H$**	 **$+\Delta H$**	
Electrostatic chemical bonding	> 40	> 200	chemisorption
Dispersion interactions and hydrogen bonding	8 - 40		physisorption
Dipole-dipole interaction	< 8	< 20	physisorption

2.2.1.1. Adsorption Isotherms

The relation between amount adsorbed and concentration is known as the adsorption isotherm. Adsorption equilibrium data is typically plotted in the form of an adsorption isotherm with the mass adsorbed on the y-axis and the mass in the fluid on the x-axis at constant temperature.

Freundlich Isotherm: A brief emprical equation often used to represent adsorption data is called the freunlich equation. The Freundlich Isotherm describes physical adsorption from liquids and can also be used for the adsorption of hydrocarbons on carboneous materials (Brev W.S., 1958)

The empirically derived Freundlich isotherm is defined as follows.

$$(x/m)=k_f\,[C_e]^n \qquad (2.1)$$

where; x/m : amount adsorbate adsorbed per unit weight of adsorbent.

C_e : equilibrium concentration of adsorbate in solution after adsorption

k_f: empirical Freundlich constant or capacity factor. (mg/g), (mol/L)

n: the Freundlich exponent.

The exponent (n), is an index of the diversity of free energies associated with the sorption of the solute by multiple components of a heterogeneous sorbent. When n=1, the isotherm is linear and system has a constant free energy at all sorbate concentrations. When $n < 1$, the isotherm is concave and sorbates are bound with weaker and weaker free energies, finally, when $n > 1$, the isotherm is convex and more sorbate presence in the sorbent enhance the free energies of further sorption. (Schwarzenbach R.P., 2003)

The good fit of freundlich isotherm to an adsorption system means there is almost no limit to the amount adsorbed and there is a multilayer adsorption. The applicability of the Freundlich equation to a particular case is tested by plotting log *(x/m)* against log [C] from the logorithmic form of Equation (Eq 2.)

$$\log (x/m) = \log k_f + n \log [C] \qquad (2.2)$$

such a plot sould yield a stright line with intercept equal to *k* and slope equal to *n*

Langmuir Isotherm: An alternative equation was derived by Langmuir on the basis of a definite case of the nature of the process of adsorption from solution. The langmuir adsorption isotherm was developed by assuming that;

1. A fixed number of accessible sites are available on the adsorbent surface, all of which have the same energy.
2. Adsorption is reversible.
3. Monolayer adsorption occurs.
4. There are no lateral interactions among the adsorbates.

The langmuir adsorption isotherm is defined as

$$(x/m)= (ak_LC_e) / (1+k_LC_e) \qquad (2.3)$$

where; x/m : amount adsorbate adsorbed per unit weight of adsorbent.

C_e : equilibrium concentration of adsorbate in solution after adsorption

a : empirical Langmuir constant which represents maximum adsorption capacity (mg/g)

k_L : empirical Langmuir constant (L/mg) (Finqueneisel G., 1998)

The a represents the total number of surface sites per mass of adsorbent. In the ideal case, ‘*a* ‘ would be equal for all sorbates. However, ‘ a ‘ may vary somewhat between different compounds because of differences in sorbate sizes. Therefore, it usually represents the maximum achievable surface concentration of a given compound. The constant k_L which is commonly referred to as the Langmuir constant is defined as the equilibrium constant of the sorption reaction. The k_L also implies a constant sorbate affinity for all surface sites. (Schwarzenbach R.P., 2003)

To applicate Langmuir isotherm, the plot of *[C]/(x/m)* against *[C]* should yield a straight line with a slope of *1/a* and an intercept of *1/ak*. The Langmuir isotherm is limited in its application to adsorption in monolayer. It applies well to chemical adsorption and to physical adsorption when saturation is approached. (Brev W.S., 1958)

The BET Isotherm: If the initial overlayer act as a substrate for further (e.g physical) adsorption then, instead of the isaturated value at high concentrations, isotherm can be expected to rise indefinetely. The most widely used isotherm dealing with multilayer adsorption was derived by Brunauner, Emmett, and Teller, and is called the BET isotherm. (Atkins, P.V., 1994)

$$q = \frac{q_m K_b C}{[\![C_a - C]\!][\![1+(K_a-1)]\!][\![C / C_a]\!]} \qquad (2.4)$$

where

q : adsorbed amount (mg/g)

C : concentration at which all layers are filled

K_b : the BET coefficient

Its assumptions are:

1. Adsorbed molecules stay put.
2. Enthalpy of adsorption is the same for any layer.
3. Energy of adsorption is the same for layers other than the first.
4. A new layer can start before another is finished.

It is important that many unusual adsorption isotherms are fitted well by the BET equation. This is to be expected when there are three coefficients to manipulate. The maximum loading, q_m just multipiles to move the entire curve up and down. The coefficient, K_b, has a major effect on shape. The concentration at which all sites are saturated (maybe several layers) can be adjusted to get a portion of the isotherm. As C approaches C_a (initial concentration), the denomenator of the equation becomes small, and the curve shoots up.

2.2.2. Phenol Adsorption on Different Substrate Surfaces

Banat *et. al.* (1999) investigated the adsorption behaviors of phenol on bentonite in aquous systems and found the effective parameters on process. These parameters were contact time, pH and inital phenol concentration. Time to reach equilibrium for the adsorption of phenol was 6 hours, which was an indication of a fast adsorption process. They also measured pH of the solution before and after adsorption and saw that there was a difference between these two pH values. This was the dependency of phenol ionization on the pH value. The efficiency of adsorption on bentonite increased with an increase in initial phenol concentration depending on the mass transfer driving force from bulk solution to the particle surface. On the other hand, the percentage of phenol adsorbed on bentonite was decreased when the initial phenol concentration increased. Adsorptive capacity of bentonite for phenol was limitted to 1 mg/g. The adsorption desorption isotherms (Langmuir and Freundlich) which were found to be good fitting for the equilibrium data indicated irreversible adsorption.

Juang *et. al.* (1999) obtained the adsorption isotherms of phenol on macroreticular resins in water using Langmuir , Freundlich and BET equations and showed that their adsorption can not be presented by the conventional such equations over the whole concentration range. The combined or modified form of BET with the Freundlich and Langmuir equations were used. Authors interpreted the sharp rise of adsorbed amount at high initial phenol concentration values as a result of multilayer adsorption. Finally, they calculated the heat of adsorption (enthalpy) as less than 45 kJ/mol which is lower than data from activated carbon in general. This value suggests that the adsorption process is between physical and chemical (transition) adsorption.

Khan *et.al.* (1997) studied the adsorption of phenolic compounds on activated carbon at different temperatures from 298 K to 424 K and found enthalpy of phenol adsorption as approximately -22 kJ/mol. This indicates that phenol adsorption on activated carbon is a physical process.

Viraraghan *et. al.* (1997) used fly ash, bentonite and 90-95 % organic matter containing peat to adsorb phenol. They found an equilibrium time as approximately 16 hours for all the adsorbent materials used. Adsorptive capacities of these materials ranged from 41.6 % to 46.1 % for the initial phenol concentration of 1 mg/L. Freundlich isotherm presented the data well for peat and bentonite and Langmuir isotherm presented tha data for fly ash.

Organoclays also have an adsorptive capacity ranging from 96 to 100 % for phenol. This removal percentage means 1 mg phenol / g organosmectits for the initial phenol concentration of 1 mg/L (Viraraghan *et. al,* 1997). Organoclays in their study were prepared from saturated high charge smectite with high organic carbon content as coal and activated carbon.

An agricultural waste, rubber seed coat activated carbon was another material used to adsorb phenol (Rengeraj S. *et. al,* 2002). Adsorption of phenol on activated carbon follows first order reversible kinetics. It is possible to reach 96 % removal efficiency after 24 hours of contact time for initial phenol concentration of 25 mg/L and carbon dosage of 0.2 g / 100 ml. (30 m^2 avilable surface area for phenol solution).

Roostai *et. al.*(2004) studied phenol with adsorption using different adsorbents such as silica-gel, activated alumina, activated carbon, and various zeolite structures. Adsorption followed a first order reversible kinetic according to the models of Freundlich and Langmuir. Silica-gel and activated alumina had no significant phenol adsorption but zeolite-Y had the fastest adsorption kinetics according to this investigation. Activated carbon reached its limiting saturation capacity during the adsorption of phenol, but very long contact time, a 10 days period, was needed to reach equilibrium. On the other hand, adsorption capacity of zeolite decreased with increasing temperature depending on the system is being exothermic.

Ugurlu et. al. (2003) found that sepiolite can be removed from paper industry wastewaters up to 80 % depending on the solution pH and activation temperature (120 ^{0}C) for 3 hours of equilibrium time. Removal efficiency of sepiolite decrease with increasing particle size also.

In another research, mechanism of phenol adsorption onto electro-activated carbon granules were investigated by Lounici et. al. (2003). Specific surface area of carbon granules was 1045 m^2/g and total ash was so low as 3.59 %. Adsorption mechanism was explained as diffusion into the inner portion, surface diffusion or pore diffusion or both for some cases. Although there was an increase of active sites and improvement of the performance of the solid, electroactivation process (-300mV, 0mV, and -600 mV) did not affect the mechanism of phenol adsorption during 30 minutes application to granular carboneous material.

TiO_2 –mounted activated carbon was an other adsorbent material for phenol removal from water. Tryba *et.al.* (2002) used Titanium Dioxide as a photo catalyst in order to hybridise photocatalytic activity of TiO_2 with adsorptive capacity of activated carbon. It was seen that, surface area of adsorbent decreased by the mounting of TiO_2. The surface area of original activated carbon used was 934 m^2/g and decreased to 483 m^2/g after heat treatment under 700 ^{0}C. Phenol removal efficiency by original activated carbon was 83 % for 6 hours equilibrium time, but 60-74 % by heat treated ones. The decrease in surface area brought change on pore-size distribution at the same time. This was the result of blocking the pores on the surface of activated carbon by the particles of TiO_2. The particles of TiO_2 became larger during heat treatment process. In the light of these results, it could be said that adsorption process strongly depends on surface area of adsorbent material.

Treated olive mill wastewater using olive-stone and solvent extracted olive pump originated activated carbon was used to remove phenol (Galiatsatou *et. al.*, 2002). Carbonization and activation temperature of these materials were 850 and 800 ^{0}C respectively. Six different activated carbons were prepared at different activation and carbonization time. Kinetic studies showed the maximum phenol removal of 73 % (85 mg/g) with an activated carbon sample which has a specific surface area of 902 m^2/g, micropore volume of 0.35 m^3/g and mesopore volume of 0.55 m^2/g. For a comperative explanation, it is important to note that the other activated carbon used in that study has 0.07 m^3/g mesopore volume and its adsorptive capacity is only 13.5 % (10 mg/g for the system). Adsorption isotherm data was fit to the linearized form of Langmuir. One of the main findings of this study was increase of adsorption capacity of carboneous material with increasing carbonyl groups.

2.3. Lignitic Coals as an Alternative Adsorbent Material

In the latter of the nineteenth century, unactivated charcoal filters were used in American water treatment plants. This was the first usage of coal in water technology. Then large volumes of granular activated carbon (GAC) were manufactured during World War I. In full scale water treatment by adsorption, activated carbon is used almost widely. Other natural adsorbents such as coal are being used in special processes after its treatment and activation steps.

2.3.1. Structure of Coal

Coal is a complex, heteregeneous rock which is composed of a number of distinct organic substances and varying amount of inorganic minerals (Ercan A., 1998). The converting process of living biomass into coal is known as coalification. In the main phase of this process, dead plant material (peat) undergoes biochemical transformation by microorganisms, chemical reaction and physical interaction-compaction. The volume of the peat reduced, in other words, its density increases. During the coalification, water content of dead plant material is decreased, and its chemistry is modified. The primary plant structural biopolymers (cellulose and lignin) are both affected that cellulose is largely degraded and lignin is chemically modified.

The most effective and noticable chemical change in this period is the differential loss of oxygen as well as hydrogen and nitrogen from the peat with respect to carbon. Additionally, the ratio of aromatic carbons to aliphatic carbons increases. Depending on the increase of depth, temperature increases, biochemical activity ceases and there is no further oxygen input. This is purely a thermodynamic process and known as catagenesis phase. During the catagenesis phase, oxygen and nitrogen continue to be lost and aromatic content of the residual organic matter continues to be reorganized through polymerization and depolymerization reactions. (Berton J. *et. al,* 2003)

The chemical structure of coal is a result of the conversion of cellulose, lignin and other plant biochemical components to a large matrix of aromatics connected by aliphatic bridges. It has aliphatic and carbonyl side chain attachments and some weakly bonded small molecular components (mobile phase). A schematic view of coal structure is provided in Figure 2.5.

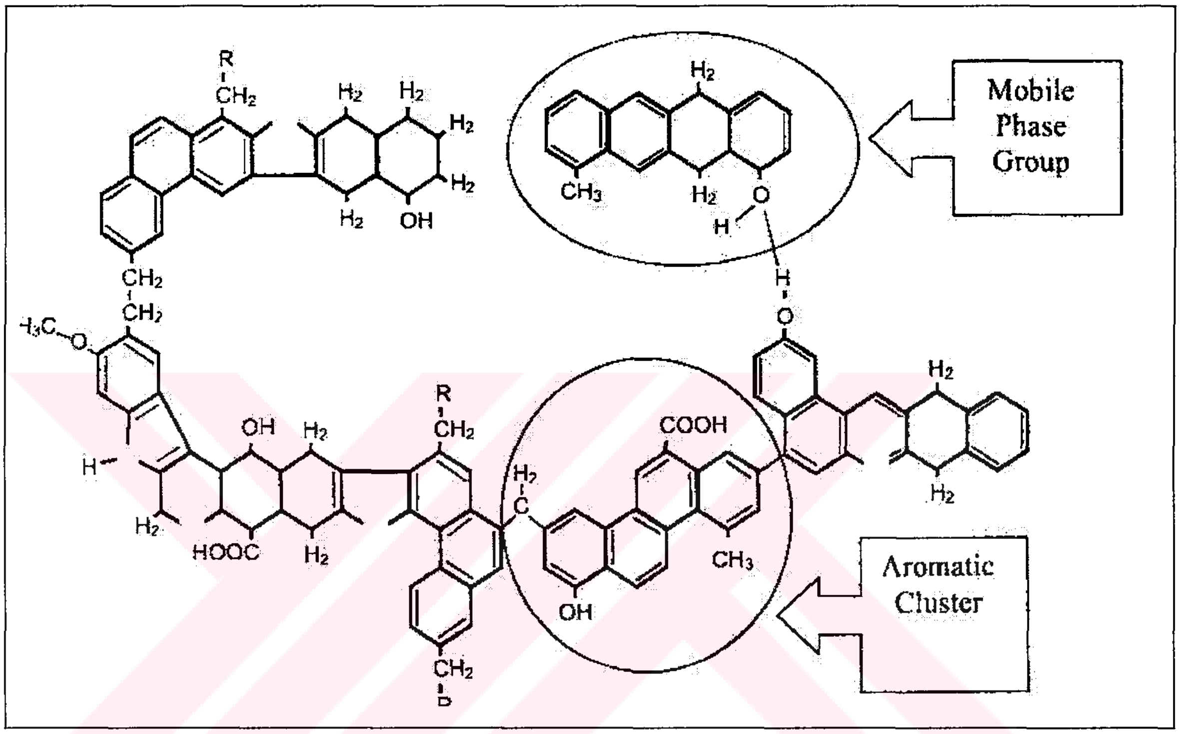

Figure 2.5. Schematic chemical structure of bituminous coal showing aromatic cluster and a mobile phase group (Berton J. et. al, 2003).

The aromatic clusters consist largely of carbon, oxygen sulphur and nitrogen. The bridges connecting to aromatic clusters are composed of aliphatic functional groups, but may also contain atoms such as oxygen and sulphur. Bridges containing oxygen have relatively weak bond strengths. Some bridges, known as char links, consist of a single bond between aromatic clusters are relatively stable. (Berton *et. al.* 2003)

According to the commercial classification, coaly materials are assigned a "rank" based on the degree to which the coalification process has proceeded. The least mature coals are lignites and the most mature coals are anthrecites. A summary information related to carbon, oxygen hydrogen and nitrogen contents of various ranks and their appearance are presented in Table 2.3.

Table 2.3. Range for Carbon (C), Oxygen (O), Hydrogen (H) and Nitrogen (N) Contents and Gross Appearance of Coals of Various Ranks (Berton J. *et. al*, 2003).

Rank	C %	O %	H %	N %	Appearence
Lignitic coal	69-76	16-25	45-60	0.1-1.75	Many plant fragments still identifiable
Sub-bituminous	67-84	11-26	3.5-7.1	0.1-2.3	Cell structure of plants largely degreaded.
Bituminous	71-92	1.2-22	3.6-7.1	0.1-2.6	Black, hard and bright; breaks into rectangular lumps
Anthracite	91-97	0.4-4.2	1.2-4.2	0.6-2.1	Black, shiny rock with charcoal fracture.

There is a wide variation in the degree of hydrophobicity of different coals due to their genesis and composition. The natural hydrophobicity may be related to rank which is one of the most common ways of classifying coal. High rank coals are hydrophobic and are characterized by high carbon (aromatic) content, density and calorific value. Hydrophlic sites on the lignite surface resulting from the aliphatic hydrocarbon content of the lignite. The hydrophobicity reaches a maxium at about 89 % carbon (law volatile and medium volatile coals are more hydropobic). In contrast; the law rank coal which contain large amounts of polar groups such as –OH, -COO, -O, -N, and –S exhibit mostly hydrophilic behaviour. When the fraction of mineral matter becomes larger, the density of the particle increases. Surface fraction of hydrophobic portion decreases.

2.3.2. The Properties of Lignitic Coals

Lignite is a mesoporous material that contain carbon less than 82 % and density of 1.4 g/cm^3 approximately. When the carbon content of the lignite decreases, density increases and porosity decreases since the pore size distribution of coal is related to the rank of the coal. Pore sizes of these mesoporous materials are between 20 A^o and 200 A^o. Depending on the particle size distribution, pore volume distribution changes.

Some fractional groups such as carboxyl, hydroxyl, etc. affects pore structure and surface area. Some physical properties of lignites are summarized in Table 2.4.

Table 2.4. Physical Properties of Lignites (as recieved)

Dielectric constant (ε)	4.7-5.3
Electrical resistance (ohm.m)	9-18
Density g/cm^3	1.2-1.5
Porosity	27-35
Moisture %	40-60
Equilibrium moisture %	35
Volatile matter %	33-62
Calorific value (kcal/kg)	1700-2700
Carbon content (avarage) %	73
Carbon content (range) %	66-76
Hydrogen content %	4.5
Oxygen content %	25-16
% Oxygen as OH %	11-7
% Oxygen as COOH %	10-6

When the moisture and mineral content of lignite increase, electrical properties become more effective. Adsorption capacity of lignite is expected to depend on the following properties listed below.

1. Lignite origin.
2. Mineral matter content and nature of ash.
3. Pore volume distribution and surface area.
4. The higher volatile matter content.

Interaction of coal with oxygen takes place thermodynamically more easily and more rapidly, compared to other gasses. So, especially law rank coals, such as lignites could easily be oxidized. Since the electronegative property of carbon is the same as sulphur, oxidation leads to important variations in the organic structure and in the properties of coal. Both the physical and chemical properties of coals except anthracite are known to sensitive to oxidation. Oxidation of coal changes elemental composition, density, specific heat, mechanical strength, floatability, functional groups, surface properties, water holding capacity etc. (Berton J. *et. al*, 2003)

2.3.3. Studies on Lignitic Coals

Lignitic coal is the most widespread energy resource in Turkey. There are 8.3 billion tons lignite reserv in 117 different regions (2 % of whole world reserv) (Ercan A, 1998 and TKI, 2002). It is possible to see lignite sources in any corner of the Turkey. This situation causes from the special geological properties. Production of lignite in Turkey is approximately 50 million tons per year. Each 7 tons lignite per 100 tons in the world are produced in Turkey. Lignite consumption in Turkey is 7 % of whole world consumption. In Turkey, all the coals except Zonguldak Coals called as lignite (lignitic coal). In general, Turkish lignites are 2-65 million years old. Turkish Lignite has high ash, high volatile matters and moisture range, law calorific value. Because of these properties of Turkish Lignite, it is not suitable for using industrial applications. In the Aegean Region, the most important lignite sources are in Kütahya, Manisa and Muğla. There are 127 million tons lignite reserves in Soma Mining Source as an example. (Özdoğan S, 1998 and TKI, 2002). 40 million tons of lignite is consumed in Turkey every year (Baba A., 2003).

A literature research based on lignitic coals were summarized in the following paragraphs.

Yaman S. *et. al,* (1999) showed the effects of oxidation on low rank lignite coal and demonstrated the changes in the chemical composition and some adsorption properties such as functional groups, porosity. Lignite was oxidized in aqueous medium at 423 K under 1.5 Mpa partial pressure of oxygen for 60 minutes. Carbon, hydrogen, nitrogen, sulphur contents of the samples (including Yeniköy Lignite) were observed to decrease under different experimental conditions. Carbon content decreased from 76.9 % to 65.5 and sulphur contamination decreased from 2.3 % to 1.0 %. Oxygen amount increased from 11.4 %, to 25.9 %. Other findings of these authors were increase of C – O, C = O, O – H groups and decrease of C – H bonds. It is important to note for this adsorption process that, pore radius of lignitic coal samples also reduced after oxidation.

The other research on effects of oxidation on adsorption properties of lignitic coals was done by Yavuz R. *et. al,* (2000). Similarly, they also showed a decrease of C – H groups and occurance of C = O functional groups after oxidation. They also noted that, initial stages of air-oxidation were characterized by chemisorption of oxygen at surface sites on the coal, and by the development of acidc functional groups such as phenolic –OH, -COOH and C = O. Adsorption efficiency is negatively affected by hyrophilic siteson the coal surface. Air oxidation of lignite makes the surface more hydrophilic due to the formation of acidic functional groups, and decreases the adsorption capacity.

Solano A.L. *et. al,* (1999) investigated the effects of mineral matter content on coal during the preparation of activated carbon. They used four different coal samples which have high ash level (>18%) and illite, kaolinite,quartz, pyrite, siderite as mineral matter. Their main aim was to decrease ash content of coal, because lower ash content means higher micropore volumes. In order to decrease ash content, they applied hydropneumatic wash treatment, HCl treatment and HF treatment. They also achieved to decrease ash level of coal by flotation technique. Feng B. *et. al,* (2001) also obtained higher surface and micropore area with a similar approach. They tried to decrease inorganic matter content of a coal char and saw an increase from 427.5 to 884.7 m^2/g for specific surface area and from 0.12 to 0.43 cm^3/g for micropore volume by heat treatment method. Also base treatmnet with KOH (Hsu L.Y. *et al,* 2000), phosphoric acid activation (Teng H. *et al,* 1997), acetic acid washing method (Sakanishi K. *et. al,* 2002) pyrolysis under nitrogen atmosphere (Skodras G. *et al,* 2002), are other effective but expensive methods on coal activation to get higher adsorptive capacity. All these methods bring additional costs on process.

There are studies in the literature to produce effective and cheap adsorbents from lignites. One of these studies was performed in a rotary kiln at 8 $^0C/min$. Final temperature was optimized between 650-850 ^0C to reach the best surface area. All experiments were done under a constant argon stream. Approximately 30 % increase (from 293 m^2/g to 400 m^2/g) were supplied on surface area of lignite originated new adsorbent comparing to the its commercial reference after pyrolysis. Finqueneised G. *et. al,* (1998) also used this new adsorbent material for nitrophenol adsorption in aqueous phase, and showed that adsorption capacity for activated lignitic coal were three times higher than natural lignite. They also demonstrated the effect of the nature of ashes which positively influences the micro and mesoporosities.

25 environmentally sensitive elements can be found in coal in appreciable concentrations. These elements are As, Ba, Be, B, Cd, Cl, Cr, Cu, F, Pb, Hg, Mn, Mo, Ni, P, Se, Sb, Ag, Tl, Th, Sn, V, U, and Zn. A large scale investigation on minor, major and trace elements in lignite coal were made by Karayiğit A.I. *et. al.* (2000). Total 13 lignite samples were analyzed in detail and three of them are from Soma, Yeniköy and Yatağan Power Plants. Smectite, illitite, kaolinite, clinoptilite, quartz, dolomite, calcite, aragonite, siderite, pyrite minerals were monitored by XRD for all lignite samples in various ranges. All major elements are ranged from 100 to 400 μg/g dry coal and trace elements from 1 to 50 μg/g dry coal.

The avarage values of trace elements in Turkish Lignite is given in Table 2.5.

Table 2.5. Trace Elements in Turkish Lignites (Ercan A, 1998).

Elements	**Avarage Value (ppm)**	**Elements**	**Avarage value (ppm)**
Cobalt	10-870	Silver	3-32
Nikel	30-2050	Zinc	30-450
Germenium	4-28	Lead	10-140
Volfram	3-110	Crom	6-2100
Galadium	6-130	Cupper	5-30
Bizmut	4-21	Uranium	4-270

CHAPTER III

MATERIALS AND METHOD

3.1. Materials and Sample Preparation

3.1.1. Lignitic Coal Samples

The lignitic coal samples used in this study were obtained from Soma and Yatağan Power Plants in Turkey.

The main characteristic properties of these coals were presented in Table 3.1 and Table 3.2 . The proximate analysis of lignitic coals were taken from the offical reports of their power plants. elemental analyses of each ones are a summary of their chemical analyses. Data of the last column of the tables were obtained from Micromeritics ASAP 2010 volumetric adsorption device.

SEM Images of Lignites can be monitored from the Figures 3.1 and 3.3. Chemical Analyses and XRD Analyses methods were also explained in detail in following sections.

3.1.2. Chemical Analyses

Coal samples were burned at 800 ^{0}C to obtain ash. Ash samples were grinded to 100 μm for chemical analyses. Firstly, 0.25 g of samples were weighted, 3 g of litium tetraborate was added into samples, and they were burned at 1100 ^{0}C for 90 minutes. Melting samples were placed in a desikator, then 100 ml HCl (10 % diluted) was added into samples and they were solved using a magnetic stirrer. Solution were diluted to 250 ml and their elemental contaminations were determined by an atomic adsorption spektrometer (Perkin Elmer 2280).

Soma Lignite

Table 3.1. Characteristic Properties of Soma Lignitic Coal (as received)

Proximate Analysis	**(%)**	**Oxides***	**(%)**	**Elements**	**mg/kg**	**Other Analyses**	
Ash	32	CaO	33.77	Pb	420.00	Surface area (BET) (m^2/g)	4.79
Volatile matter	16-35	SiO_2	33.41	Cu	172.00		
Fixed carbon	11.34	Al_2O_3	16.13	Ni	152.00	Micropore area (m^2/g)	7.71
Moisture	21	Fe_2O_3	6.00	Zn	116.00		
		MgO	6.07	Co	104.00	Mean pore diameter (A^0)	8.35
		SO_3	2.80	Cr	64.00		
Quality Analysis (kcal/kg)		Na_2O	1.04	Sr	60.00		
Calorific value	2200	K_2O	0.66	Cd	40.00	Nominal particle size, µm	250
		BaO	0.15				

(Akar. G., 2001)

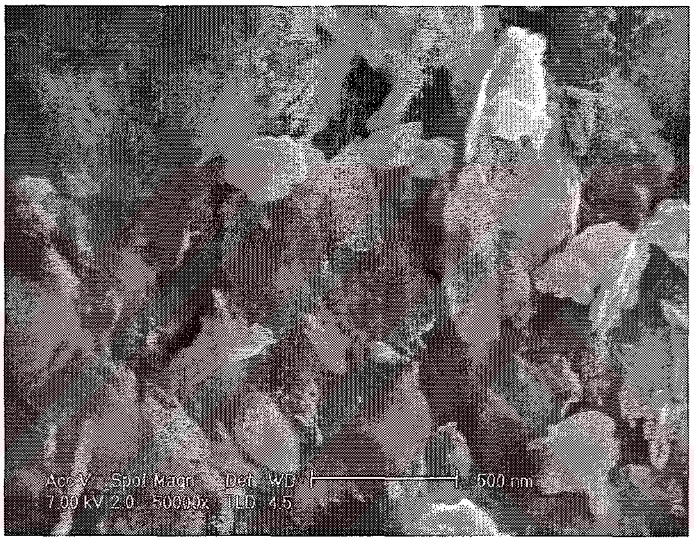

Figure 3.1. SEM Image of Soma Lignitic Coal

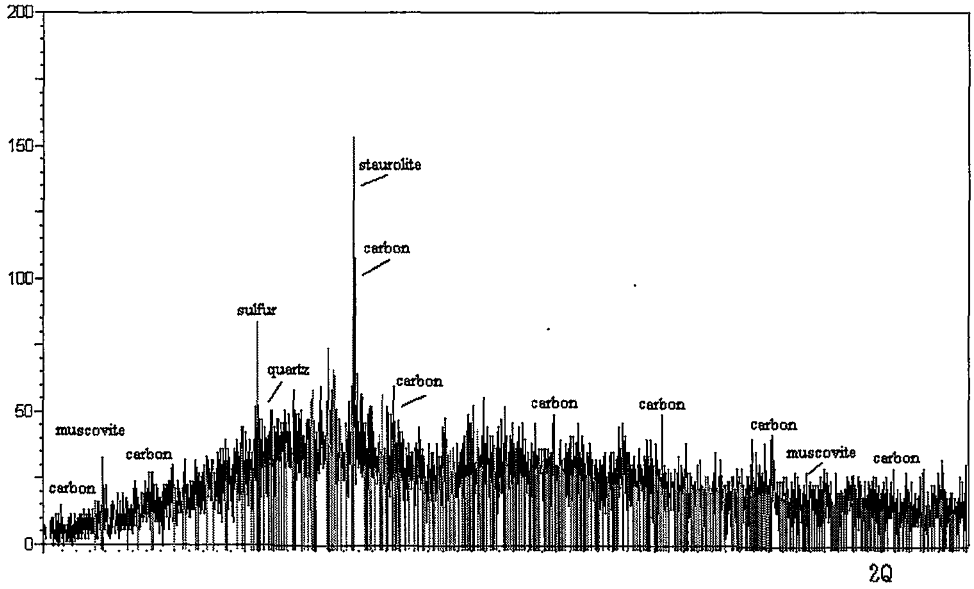

Figure 3.2. XRD- Mineralogical Analysis of Soma Lignitic Coal

Yatağan Lignite

Table 3.2. Characteristic Properties of Yatağan Lignitic Coal (as recieved)

Proximate Analysis	**(%)**	**Oxides***	**(%)**	**Elements**	**mg/kg**	**Other Analyses**	
Ash	28-35	CaO	33.77	Pb	391.84	Surface area (BET) (m^2/g)	7.15
Volatile matter	> 25	SiO_2	36.43	Cu	179.93		
Fixed carbon	18.50	Al_2O_3	16.13	Ni	163.93	Micropore area (m^2/g)	4.33
Moisture	32-40	Fe_2O_3	7.77	Zn	119.95		
		MgO	8.80	Co	95.96	Mean pore diameter (A^0)	40.2
		SO_3	6.83	Cr	91.96		
Quality Analysis (kcal/kg)		Na_2O	1.05	Sr	43.98		
Calorific value	2100	K_2O	0.77	Cd	31.99	Nominal particle size, µm	320
		BaO	0.15				

(Akar. G., 2001)

Figure 3.3. SEM Image of Yatağan Lignitic Coal

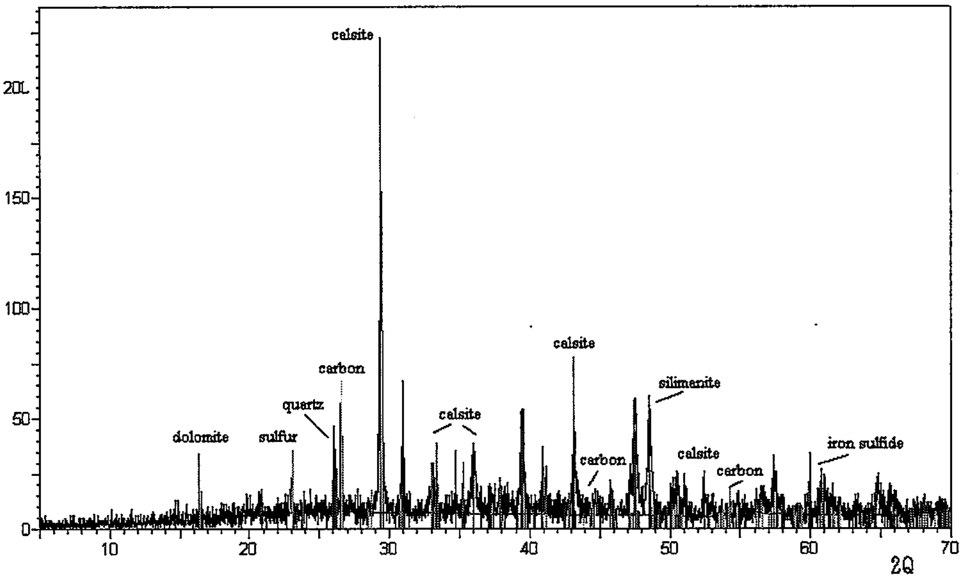

Figure 3.4. XRD- Mineralogical Analysis of Yatağan Lignitic Coal

3.2. Double Distilled Water

Double distilled water which was passed through Barnstead Easypure UV-Compact ultrapure water system (18.3 ohm) was used to prepare all solutions. Glasswares were cleaned with nitric acid, and the acid was washed using distilled water.

3.3. Reagents

In order to prepare phenol solutions during the experiments, phenol which obtained from the MERCK Chemical Company (a molecular weight of 94.11 g/mole with a vapor pressure of 0.41 mm Hg at 25 °C) was used. A known amount of phenol was taken and it was soluted in a 1000 ml of distilled water for each experiment sets. After the phenol solution prepared, volumetric flask which contain phenol solution was placed in a magnetic stirrer for 30 minutes to obtain homogen phenol solution. Stock solutions were prepared dailiy and were kept in a refrigerator at about 20 °C.

To investigate the effect of some major elements and heavy metals on removal of phenol, $CrCl_3$, $Co(NO_3)_2$, $Cu(NO_3)_2$, (Sigma Chemical Company) $Pb(NO_3)_2$ $Zn(NO_3)_2$, (Aldrich Chemical Company), and $HgCl_2$, (Horasan Chemical Company) were used. These solutions were prepared as 10 mg/L for each experiment set.

Metal concentrations in solutions and their species at experiment pH (pH=8.0) were given in Table 3.3.

Table 3.3. Speciation for Cr (III), Hg (II), Co (III), Cu (II) , Pb (II) and Zn (II) in contact with their hydroxides. (*ionic strength is zero, pH = 8.0*)

Compounds (10 mg/L)	Metal Concentrations		% of Total Component Concentration	
	ions	mg/L	Species Name	%
$CrCl_3$	Cr^{3+}	3.28	Cr^{2+}	0.12
			$[Cr(OH)]^+$	99.88
$HgCl_2$	Hg^{2+}	7.40	Hg^{2+}	100.00
$Co(NO_3)_2$	Co^{2+}	4.75	Co^{2+}	97.88
			$[Co(OH)]^+$	1.96
			$Co(OH)_2$ (aq)	0.16
$Cu(NO_3)_2$	Cu^{2+}	3.42	Cu^{2+}	7.04
			$[Cu_3(OH)_4]^{2+}$	49.32
			$[Cu(OH)]^+$	22.40
			$[Cu_2(OH)_2]^{2+}$	17.08
			$Cu(OH)_2$ (aq)	4.14
			$[Cu(OH)]^{3-}$	0.02
$Pb(NO_3)_2$	Pb^{2+}	6.25	Pb^{2+}	27.50
			$[Pb(OH)]^+$	69.53
			$Pb(OH)_2$ (aq)	2.22
			$[Pb_3(OH)_4]^{2+}$	0.73
			$[Pb_2(OH)_3]^{3+}$	0.02
$Zn(NO_3)_2$	Zn^{2+}	3.47	Zn^{2+}	81.41
			$Zn(OH)_2$ (aq)	10.39
			$[Zn(OH)]^+$	8.20

3.4. Experimental Methods

3.4.1. Characterization Studies for Lignitic Coals

3.4.1.1. Sample Preparation and Determination of Size Distribution

Coal samples were taken directly from coal stocks of the power plants as approximately 100 kg for each one without any pretreatment. Samples were air dried and later crushed in a laboratory jaw crusher-hammer mill-screen setup down to a size of –500 µm. Representative samples of 250 g were obtained by appropriate sampling method. Representative lignite samples were placed into a size screen analyser (Retsch S1000) to determine size distributions of particles.

3.4.1.2. SEM , EDX and XRD Analyses

The pictures of pelleted lignitic coal particles were taken by a scanning electron microscope (SEM, Philips XL 30 S FEG). Quartz, staurolite, muscovite, dolomite, silimanite, calcite, calcium carbonate, calcium magnesian and staurolite minerals were detected in the XRD analysis of samples by an X-RAY Diffractometer (Philips X'Pert Pro). Mineral contamination of two lignitic coal samples which were detected from X RAY Diffractometer were summarized in chapter 4 (Table 4.1).

In the EDX analyses, 10 readings on each pelleted coal sample were carried out at regular intervals on separate samples. At the end, a total of about 100 readings were done. The results give the avarage of these readings. A summary of the EDX results with standard deviations were given in chapter 4 (Table 4.2).

3.4.1.3. Zeta Potential Measurements

In order to have an idea about pozitive or negative charge distribution on lignite surfaces, in other words, potential difference across the difuse part of the electrical double layer at surfaces, zeta potential measurements were carried out using a Zeta Sizer Measurement Device 3000 HS from Malvern. Before the measurements, lignite samples were grinded into the size below 38 µm and 0.1 g of samples were added into 100 ml double distilled water. Lignite solutions were kept in a Memmert Model Ultrasonic Bath for 10 minutes and 10 times diluted solutions were injected into measurement device.

3.4.1.4. Surface Area Analyses

All lignitic coal samples were analysed by Micromeritics ASAP 2010 volumetric adsorption device to investigate adsorption properties and porous properties before the batch adsorption studies. Adsorptive gas was nitrogen during the analyses and temperature was constant as 77 K for all coal samples. The working principle of volumetric adsorption measurement device based on monitoring nitrogen gas adsorption (or desorption) on to (from) solid surface at a constant temperature during the interval time. Adsorbed nitrogen gas volume (V_A) as cm^3/g was measured at each pressure, and adsorption isotherms were obtained as a function of V_A and relative pressure (P/P_0). Surface area of solid are calculated using model equations as m^2/g.

3.4.1.5. Adsorption Studies

The kinetic batch adsorption studies were conducted at room temperature (25± 1 °C) and at natural pH of 8.0 of the coal - water solution unless otherwise is stated. A Memmert Model Ultrasonic Bath was employed to adjust temperature when it is necessary. A 250 ml bottle with a known amount of coal sample and 100 ml phenol solution of known initial concentration was placed on an IKA Labortech-KS125 digital shaker and run at 600 rpm mixing speed. Aliquots of samples were taken from these suspensions at preset time intervals of 5, 20, 90 minutes, 3, 6, 24, 48, 96 and 168 hours. To withdraw liquid from suspensions, a series of Macherey Nagel type (40x40) filter paper with a vacum system and syringe filters from Sartorius Minisart RC 25, 0.45 µm were utilized. For each time, a different sample bottle was used to ensure that the solid / liquid (S/L) ratio did not change after sampling. The supernatant solutions were analyzed for phenol determination with a UV Spectrophotometer (UV-VIS 1208 from Shimadzu) at 270 nm according to calibration curves obtained.

3.5. Determination of Water Quality

3.5.1. Leaching of Lignitic Coals

Leaching of coal was determined using the Standard Method ASTM D-4793. Coal samples were placed in double distilled water (S/L= 0.05) at natural pH and shaked on an IKA Labortech-KS125 digital shaker for 24 hours at 600 rpm mixing speed. To withdraw liquid from suspensions, a series of Macherey Norgel type (40x40) filter paper with a vacuum system and syringe filters from Sartorius Minisart RC 25, 0.45 µm were utilized. The supernatant solutions were analysed by an ICP (Inductively Coupled Plasma-Atomic Emission Spectrophotometer) from Varian, AES Axial Liberty Series 2. 0.2 ml of nitric acid was added into each supernatant solutions (20 ml) to prevent sedimentation of heavy metals and major elements before the multielement analysis. Multielement stock solution (ICP multielement standard solution IV from MERCK Company; 1000 mg/L Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn) prepared daily at least three different concentration for each time to get calibration curves.

3.5.2. Determination of Organic Matters

For the determination of organics, a known amount of coals were weighed. Before the extraction, coals were kept under oil bath – vacuum system for 48 hour at 100 °C in order to remove all moisture and then weighed again. The samples were then treated in a Soxhlet evaporator-condanser set-up where the coals were subjected to dissolution by a limited amount (500 ml) of recycling distilled water to prevent reversible dissolution of dissolvable species for 24 hours at 100 °C. After the reaction the treated coal samples were dried in an oil bath-vacuum system for 24 hours at 100 °C and weighed to determine the dissolved amount.

CHAPTER IV

RESULTS AND DISCUSSION

4.1. Characterization Results of Lignites

4.1.1. XRD and EDX Analyses

Mineral contamination of two lignitic coal samples which were detected from X RAY Diffractometer were summarized in Table 4.1. and EDX results of Soma and Yatağan lignitic coals were given in Table 4.2.

Table 4.1. XRD Analyses of Lignite Samples

Soma Lignite	**Yatağan Lignite**
Muscovite	Kyanite
Staurolite	Calcium carbonate
Quartz	Calcite magnesian
Carbon	Quartz
	Carbon

Table 4.2. EDX Results of Lignite Samples

SOMA LIGNITE		**YATAĞAN LIGNITE**	
EDX Analysis	Atomic (%)	EDX Analysis	Atomic (%)
Carbon	41.50±6.1	Carbon	59.10/±1.2
Oxygen	27.80±2.3	Oxygen	18.50±1.0
Sulphur	0.30±0.1	Sulphur	0.50±0.1
Aluminium	3.00±1.0	Aluminium	1.40±0.08
Magnesium	0.50±0.1	Magnesium	0.30±0.04
Calcium	4.70±1.1	Calcium	1.00±0.2
Others	22.2	Others	19.2

4.1.2. Particle Size Distributions

Figure 4.1. illustrates the cumulative particle size distributions of Soma and Yatağan lignite samples after screen analyses. The nominal particle size (k) were found to be 250 and 320 for Soma and Yatağan lignites respectively. 100% of all lignite samples were under 500 μm. and adsorption experiments were carried out using particle sizes below 500 μm.

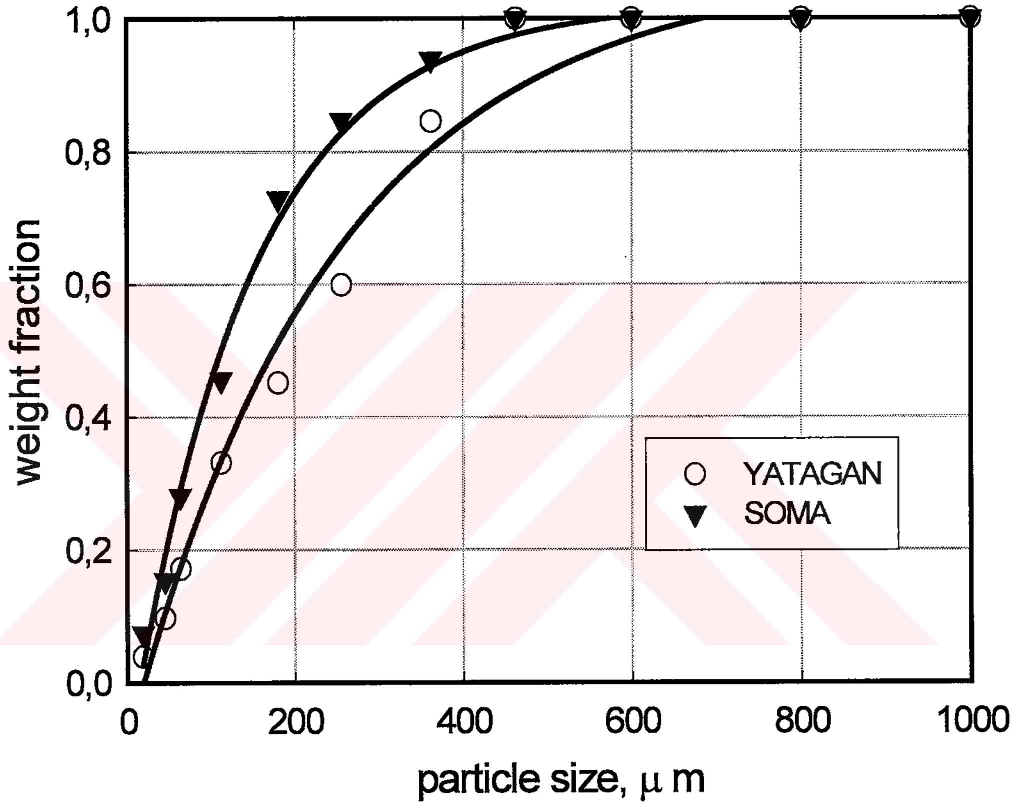

Figure 4.1. Cumulative size distributions of Soma and Yatağan lignitic coals

4.1.3. Surface Area Analyses

Figure 4.2. shows the Nitrogen adsorption isotherms of two different lignite samples. Adsorption isotherm of Yatağan lignite are concave to the P/P^O axis and then almost linear. It indicates the formation of an adsorbed layer whose thickness increases progresively with incrasing relative pressure until P/P^O is equal to 1. When the equilibrium pressure equals the saturation vapor pressure, the adsorbed layer becomes a bulk liquid or solid. These kinds of isotherms are called to be Type II-b Isotherms

accrding to the IUPAC classification and obtained with non-porous or macroporous adsorbents (Rouquerol F., 1999).

In contrast to Yatağan lignite sample, N_2 adsorption rate decreased with increasing saturation pressure (P^O) for Soma lignitic coal. Adsorbed amount of N_2 was much less and this situation indicated that, Soma lignite sample was not microporous or mesoporous but it mihgt be macroporous in nature.

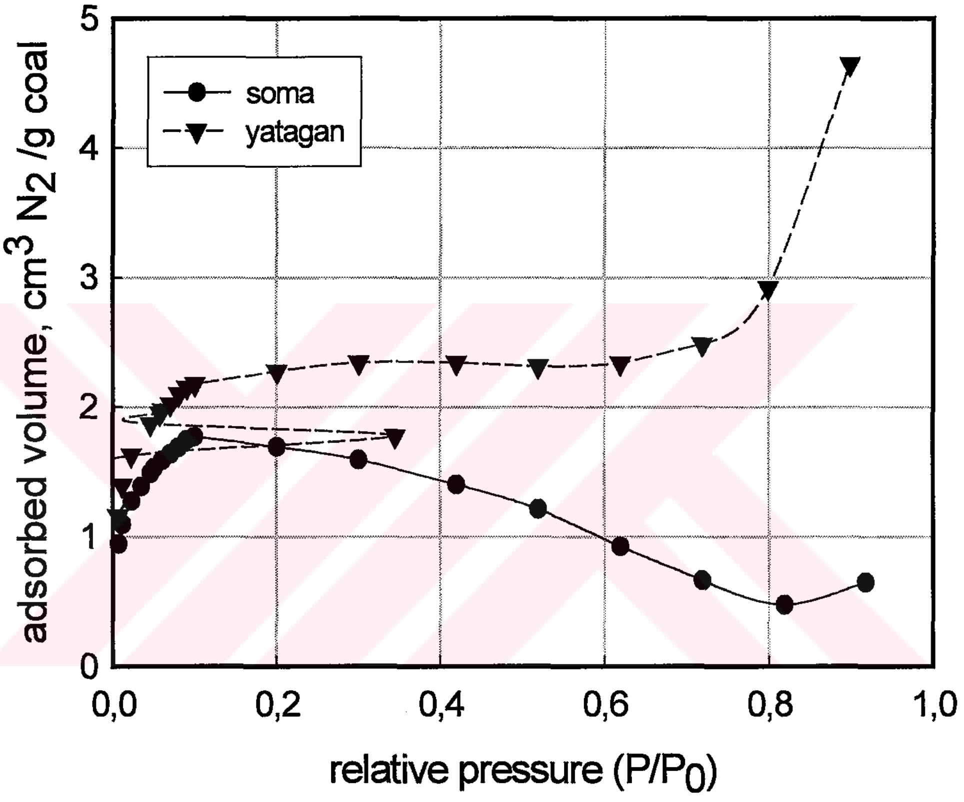

Figure 4.2. N_2 adsorption isotherms for lignitic coal samples.

4.1.4. Zeata Potential Distributions

Zeta potential distributions (Figure 4.3) were obtained at natural pH for lignitic coals surfaces and seen that the mean zeta potential values for both two lignite samples were negative (-14.00 mV for Soma and -15.27 mV for Yatağan lignites). In other words, both of the lignite surfaces are negatively charged at pH = 8.0.

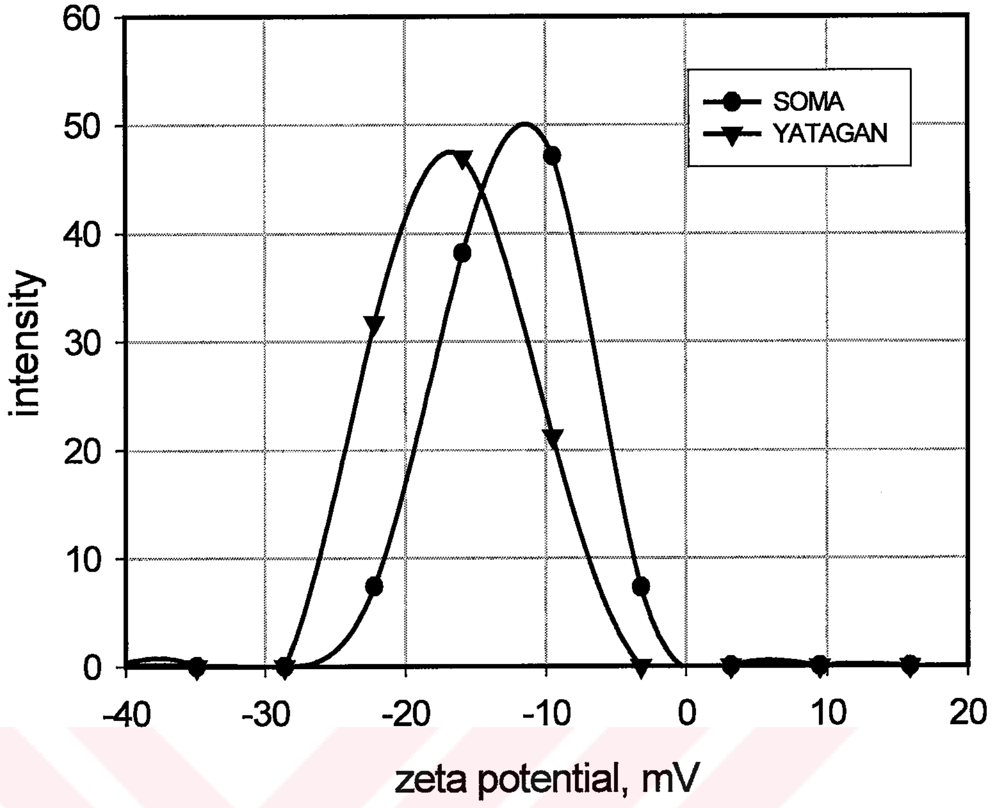

Figure 4.3. Zeta potential distributions of Soma and Yatağan lignitic coals (pH =8.0)

4.2. Phenol Adsorption on Lignite: Adsorption Capacity

An initial study was carried out to determine the phenol loss from the reaction vessel at prolonged reaction times using blank (no solids) 100 ppm phenol solutions (a different bottle for each time). It was observed that there were no phenol loss from the system as can be seen from Figure 4.4. This data also shows the reproducibility of the test and analysis procedure.

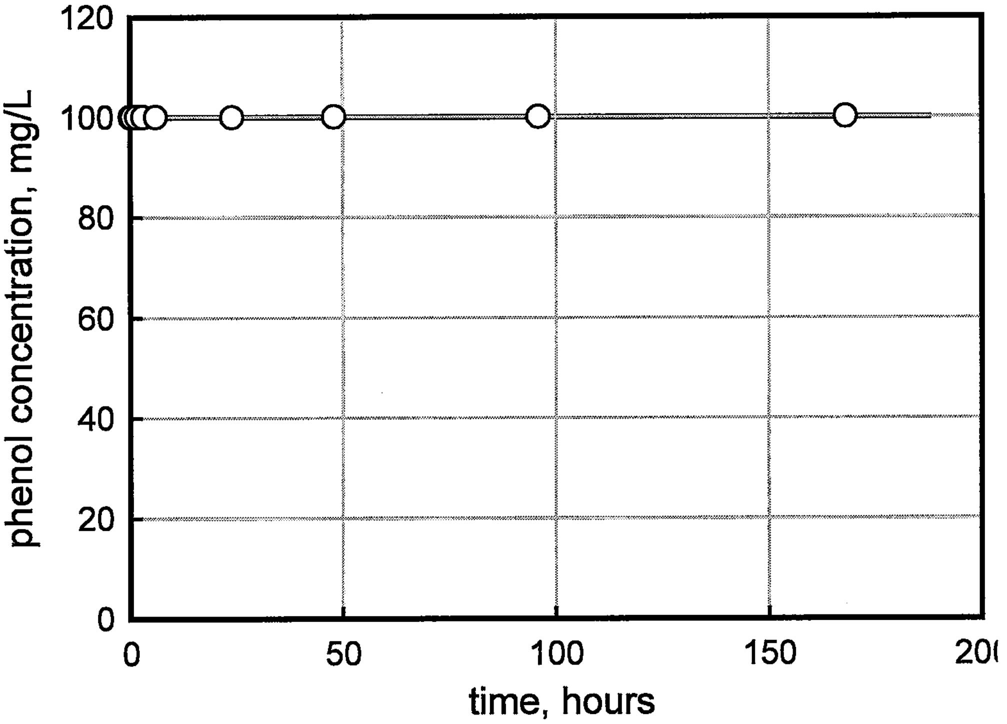

Figure 4.4. Evaporation of phenol from adsorption vessels for various reaction times.

Adsorption studies with 100 ppm phenol solutions were conducted in the presence of solids to determine the adsorption capacity of the lignite at various S/L ratios. The removal of phenol as a function of reaction time at different S/L ratios for Soma lignitic coal is given in Figures 4.5 and 4.6 in terms of percent phenol removed and mg phenol removed per gram of coal, respectively. It is seen that phenol removal by the lignite increases with increasing reaction time and increasing S/L ratio. It should be noted, however, that there is a limiting removal value for a given S/L ratio. For example, no matter how long the reaction time, the maximum phenol removal that can be achieved by S/L ratios of 0.0125, 0.025, 0.05 are 33.5%, 51.2% and 70.1%, respectively.

Complete phenol removal seems to be achievable for S/L ratios of 0.2 and 0.4 only. On the other hand, amount of phenol removed per gram of coal decreases as S/L ratio increases as expected (Figure 4.6).

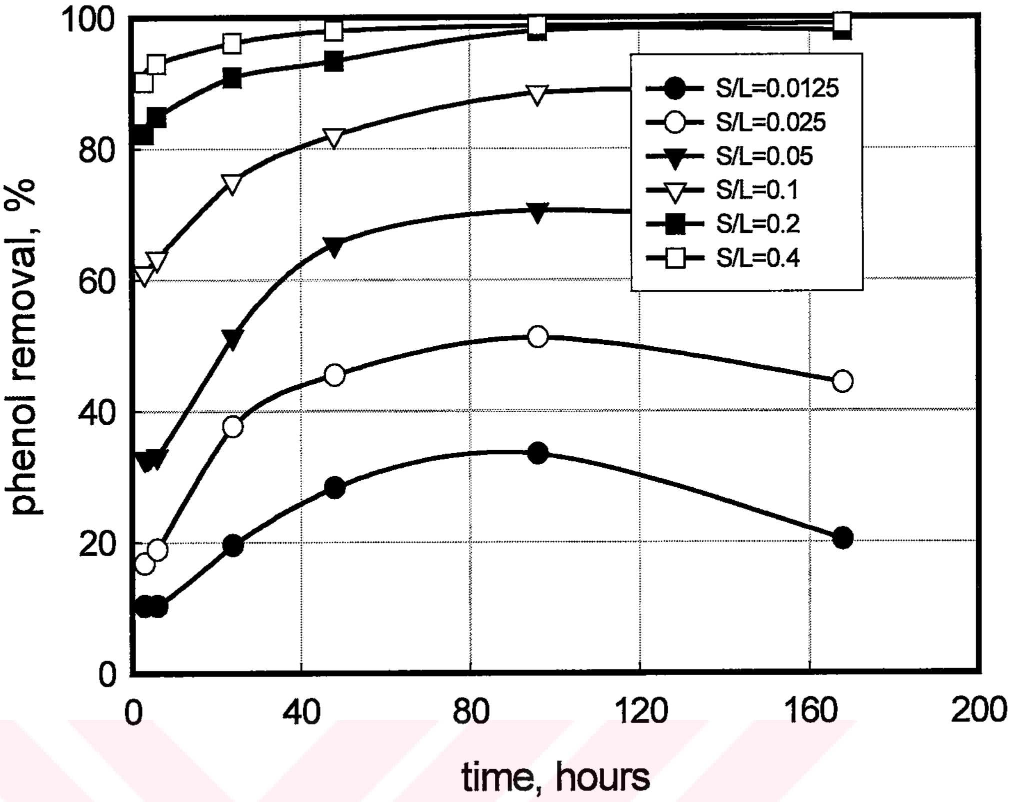

Figure 4.5. Phenol removal by Soma lignitic coal as a function of time at different S/L ratios. (initial phenol concentration: 100 mg/L; pH: natural, temperature: 298 K)

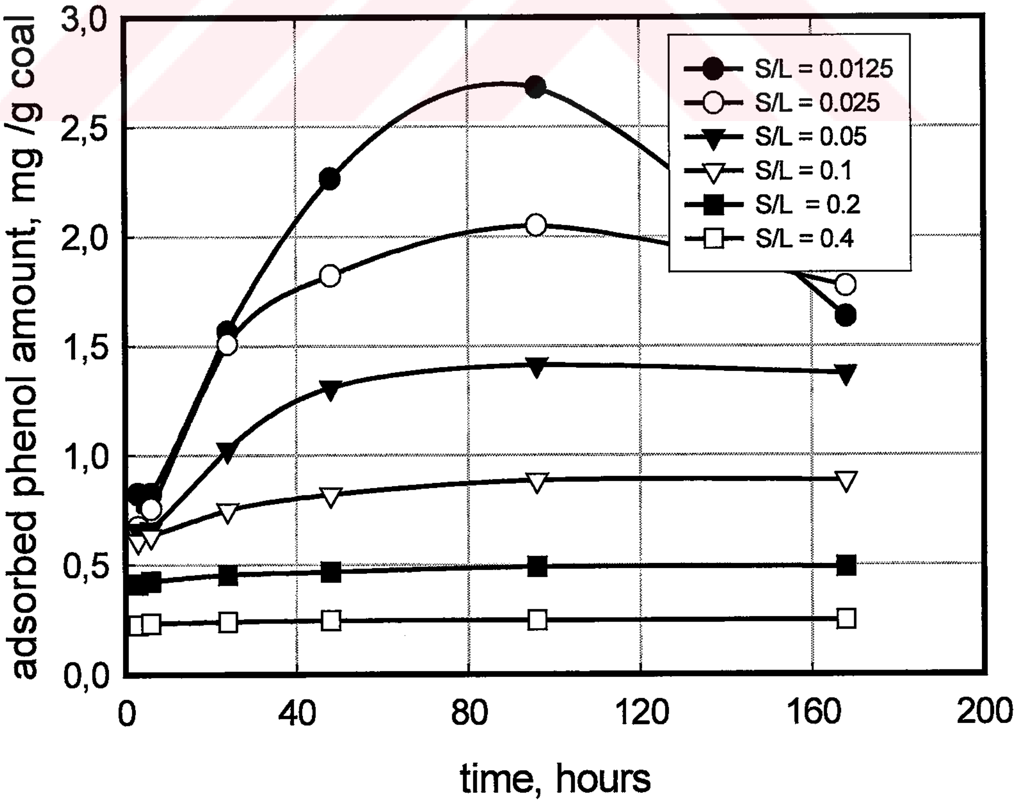

Figure 4.6. Phenol adsorbed amount by Soma coal as a function of time at different S/L ratios. (initial phenol concentration: 100 mg/L; pH: natural; temperature: 298 K)

In Figure 4.7, the data for 6, 24, 48 and 96 hours in Figure 4.5 is presented in another form. In this figure an available surface area based on the amount of coal present in solution is calculated and used bottom x-axis, assuming an average coal surface area. The top x-axis shows directly the solid amounts. In the y-axis is given the % of phenol removed from the solution. However, the data is given for each removal time as a function of the S/L ratio. It could be seen that for a given reaction time phenol removal inreases steadily as the S/L ratio increases such that complete removal could be achieved for all times if the S/L ratio is high enough. On the other hand, if the discussion for Figure 4.5. is referred, there is a maximum phenol removal capacity for a given S/L ratio. According to Figure 4.5. it will be reasonable to assume that maximum removals can be achieved at around 96 hours. Hence, as can be seen from Figure 4.7., the data for 96 hours of reaction is given differently with filled symbols and a thicker line to emphasize that every removal value on this line is the maximum removal capacity and can be interpreted as the limiting adsorption capacity for this coal with respect to phenol adsorption.

In order to elucidate the figure, one could do an approximate calculation; the number of phenol molecules in 100 ml solution (phenol concentration is 100 ppm) is about $6.4\text{x}10^{19}$. For a parking area of 30.5 A^2 for the phenol molecules (Juang R.S. *et. al*, 1999), this number of phenol molecules in solution will require a surface area of 19.5 m^2 if monolayer coverage is assumed. For each S/L ratio, this 100 ml solution contains 40 (S/L=0.4), 20 (S/L=0.2), 10 (S/L=0.1) 5 (S/L=0.05), 2.5 (S/L=0.025) and 1.25 (S/L=0.0125) grams of coal. The surface areas by BET is 4.8 m^2/g and the micropore area is 7.7 m^2/g. Assuming these numbers represent the minimum and maximum limits for surface areas for the lignite and, as an approximation, if we take the aritmetic avarage of these values, we find available surface areas of 243.2 m^2, 121.6 m^2, 60.8 m^2, 30.4 m^2 , 15. 2 m^2 and 7.6 m^2 for the respective S/L ratios given. The removal % values in the figure are plotted at these surface areas

Restating that, the bottom axis is taken as the available coal surface area based on these values, it could be seen that the required surface area of 19.5 m^2 for the given phenol concentration becomes comparable to the available coal surface areas in solution. The S/L ratio of around 0.03, which corresponds to the available surface area of 19.5 m^2 in the lower x-axis should be sufficent to remove all the phenol assuming all the lignite surface is receptive for phenol adsorption. However, it is reasonable to say that the whole lignite surface may be not receptive for adsorption most probably due to varying affinities of various sites for the phenol molecules.

The removal value read-off from the removal curve for 96 hours where the solid line drawn from 19.5 m^2 surface area value intercepts it should give the precentage of the lignite surface which is receptive to phenol adsorption for the experimental conditions studied. This value is very close to 60%, suggesting that out of the available lignite surface only about 60% is comprised of those sites useful for phenol adsorption.

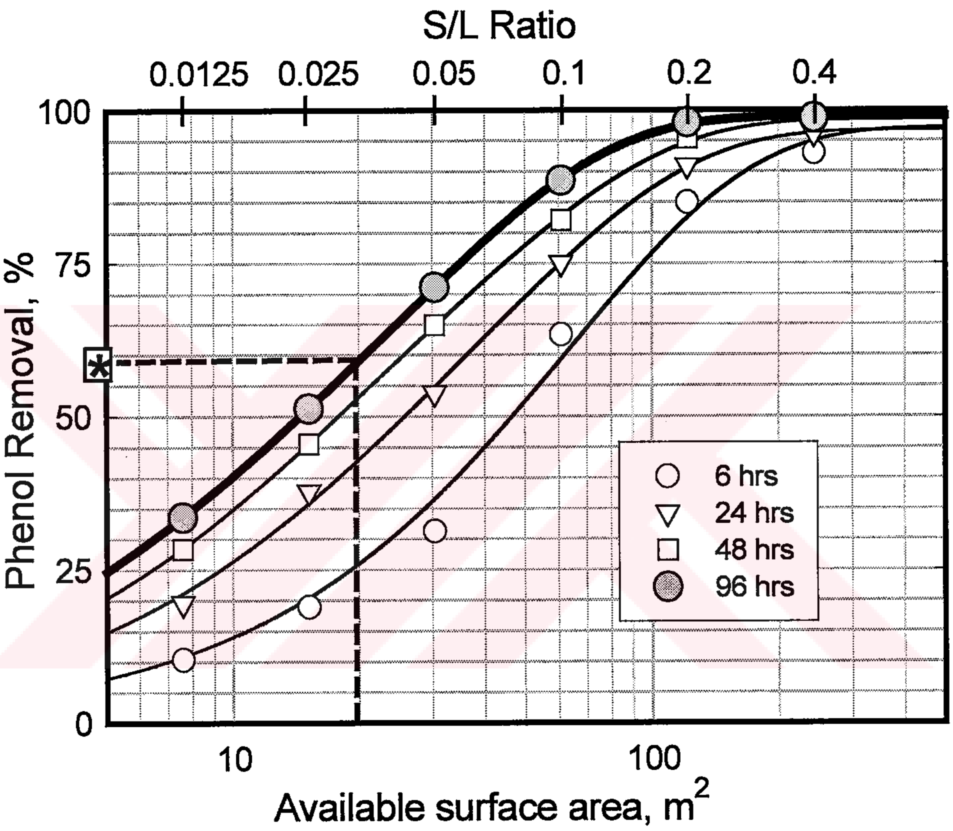

Figure 4.7. Maximum phenol removal capacity of Soma lignitic coal for various S/L ratios. (initial phenol concentration: 100 mg/L, pH: natural, temperature: 298 K)

Similar type of experiments were also conducted and data analysis were done for another lignitic coal and the results were presented in Figures 4.8., 4.9 and 4.10. It is seen from Figure 4.10. that the useful surface sites for phenol adsorption was found to be 43% for Yatagan coal.

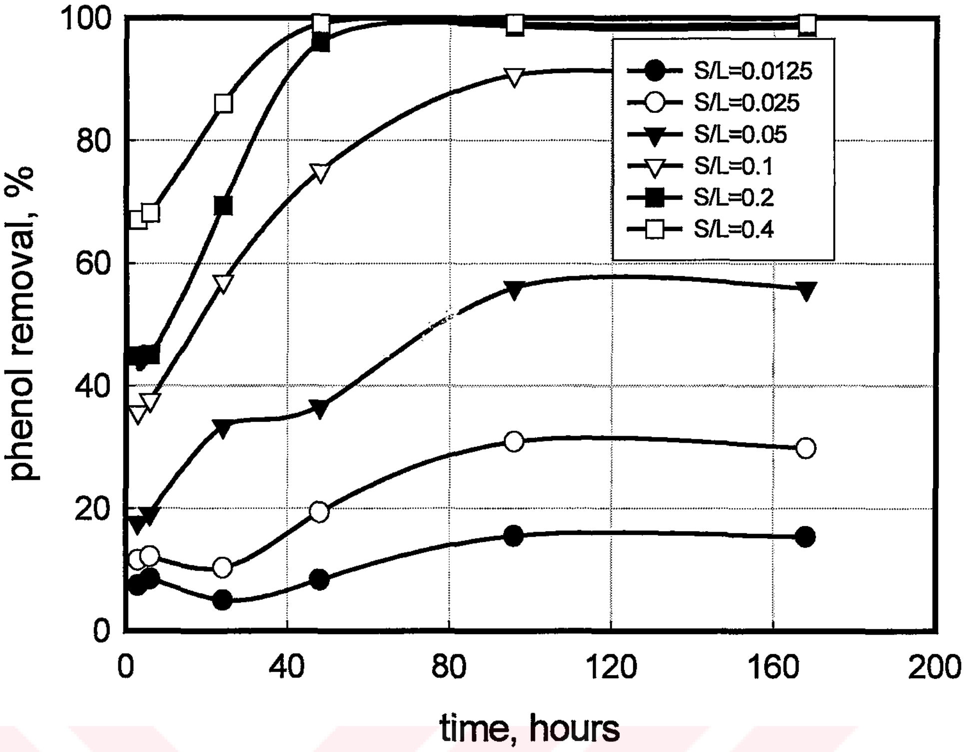

Figure 4.8. Phenol removal by Yatagan lignitic coal as a function of time for different S/L ratios. (initial phenol concentration: 100 mg/L; pH: natural, temperature: 298 K)

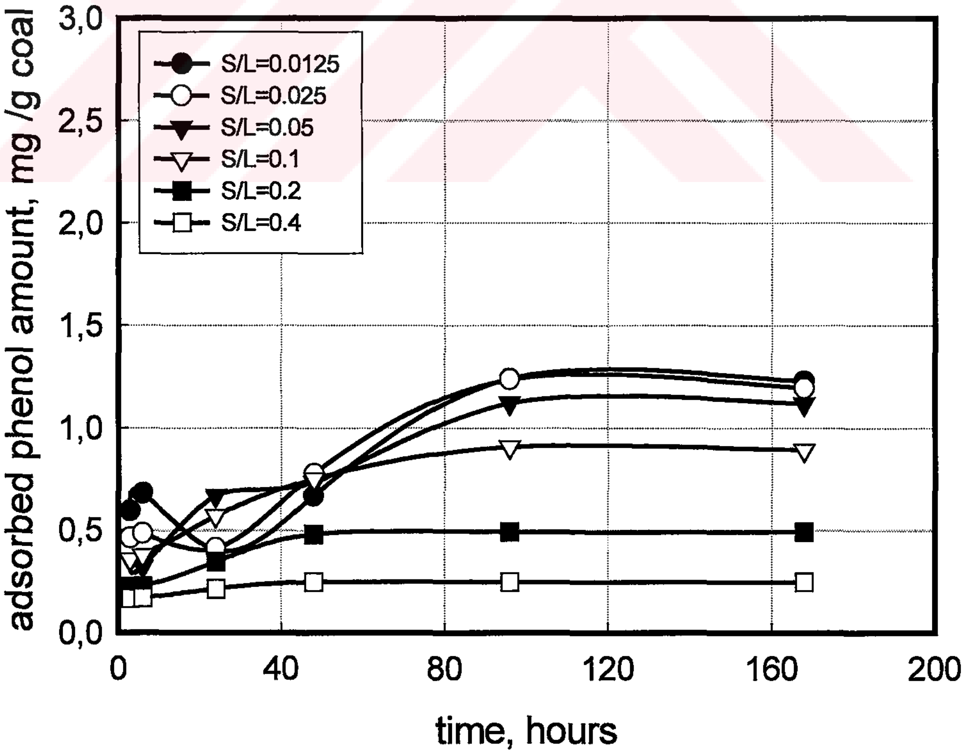

Figure 4.9. Adsorbed phenol amount by Yatagan coal as a function of time for different S/L ratios. (initial phenol concentration: 100 mg/L; pH: natural; temperature: 298 K)

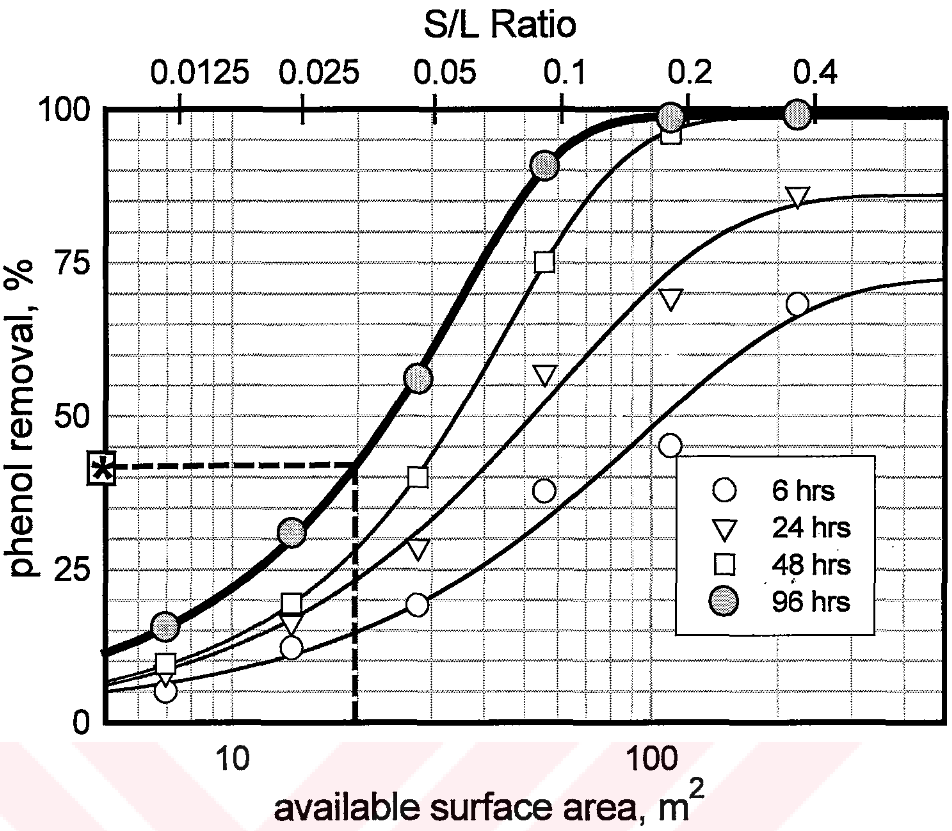

Figure 4.10. Maximum phenol removal capacity of Yatagan lignitic coal for various S/L ratios (initial phenol concentration: 100 mg/L, pH: natural, temperature: 298 K).

The results given above suggest that only a fraction of the lignite surface is available for adsorption and contributes to the removal. The reasons for this could be several. The lignite samples used in this study is a heterogeneous substance consisting of ash-forming minerals and organic matter. These low rank coals are expected to contain large amounts of polar groups such as –OH, -COO, -O, -N, and –S and exhibit mostly polar (hydrophilic) behaviour. Hence, the contribution of mineral matter or the polar groups, or the aliphatic non-polar part of the coal, on the adsorption is not clear.

In the following paragraphs, the calculation of activation energy and the heat of adsorption will be discussed to test the adsorption of phenol on this lignitic coal was through physical or chemical interactions. (Yin G. *et al*, 2002 and Atkins W.,1994)

4.3. Adsorption Kinetics and Mechanim

Kinetic adsorption studies were conducted at different temperatures of 298, 303, 308 and 313K.

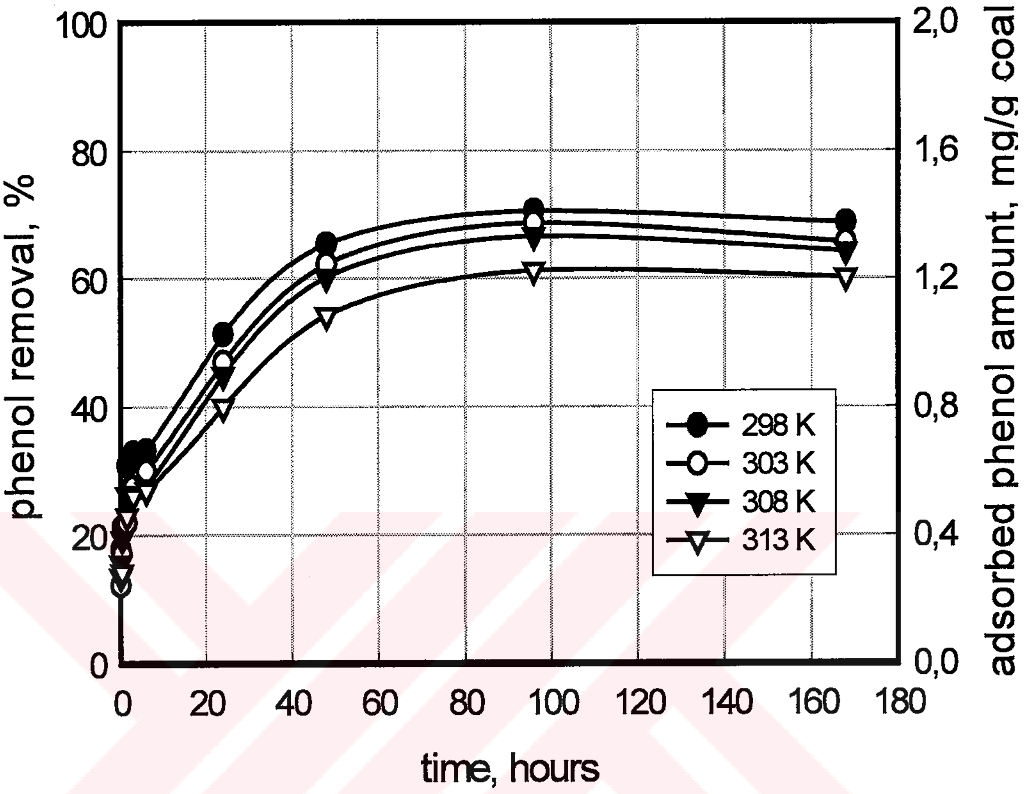

Figure 4.11. Effect of temperature on adsorption of phenol for Soma lignite (initial phenol concentration: 100 mg/L, S/L=0.05, pH: natural, temperature: 298 K)

The results presented in Figure 4.11 as the removal efficiency of phenol and the miligram phenol adsorbed per gram of coal as a function of time for different temperatures. For the Soma sample, the results indicated that, altough the adsorption of phenol decreases with increasing temperature, the effect was small.

According to Sirichote O. *et. al,* 2001, slight decreases in adsorption with increasing temperature indicate that adsorption process is exothermic and mainly physical. The maximum removal efficiency obtained decreased from 70% (1.41mg/g) to 61% (1.22 mg/g) with an increase in temperature from 298 to 313 K. The final concentration of phenol after 168 hours of contact time found to be 39.85 mg/L for 313 K; this value was 31.31 mg/L for 298 K. Each 5 K increase of the temperature affected adsorption process almost at the same rate for all the contact times.

4.3.1. Application of Adsorption Isotherms

Freundlich and Langmuir isotherms are commonly used to describe the adsorption characteristics of activated carbons utilized in water and wastewater treatment. Therefore, adsorption data of Soma lignite at 298 and 308 K were employed to test Freundlich and Langmuir models in this study.

Freundlich Isotherm

The empirically derived Freundlich isotherm is defined as follows.

$$(x/m)=k_f.[C_e]^n \qquad (4.1)$$

where;
x/m : amount adsorbate adsorbed per unit weight of adsorbent.
C_e : equilibrium concentration of adsorbate in solution after adsorption
k_f : empirical Freundlich constant or capacity factor. (mg/g), (mol/L)
n : the Freundlich exponent. (Brev W.S., 1958)

In testing the isotherm, the adsorption data is plotted as log (x/m) versus log (C_e) and should result in a stright line with slope n and intercept k_f. The intercept and the slope are indicators of adsorption capacity and adsorption intensity, respectively.

The adsorption data which was obtained for an S/L ratio of 0.05 at neutral pH were plotted for two temperatures (298 and 308 K) in the log-log form in Figure 4.12 to determine the applicability of the Freundlich isotherm to phenol adsorption on Soma lignite

It can be seen that the data shows a nearly perfect linearity which is an indication of good fit of Freundlich isotherm. This means that, adsorption steadily increases with increasing initial concentration and is not limited to monolayer adsorption. The fitting parameters in Figure 4.12 are n=0.86 k_f= 0.0268 for 298 K and n=0.83 k_f= 0.0305 for 308 K which are very close to each other as should be expected. If we take average of the very close parameters for the two temperatures, we find n= 0.845 and k_f=0.0265. The fact that, the effect of temperature is very small on Freundlich parameters, also suggest thatadsorption is not very dependent on temperature and should be dominated mostly by physical interactions; though some chemical interactions are also possible

(Sirichote O. *et al,* 2001). The small n value of 0.865 means that phenol was bound to the lignite surface rather weakly, indicating physical adsorption (Schwarzenbach R.P., 2003). Also a very small value of k_f (0.0265) indicate that the adsorption capacity of the lignite for phenol is not very high .(Schwarzenbach R.P., 2003).

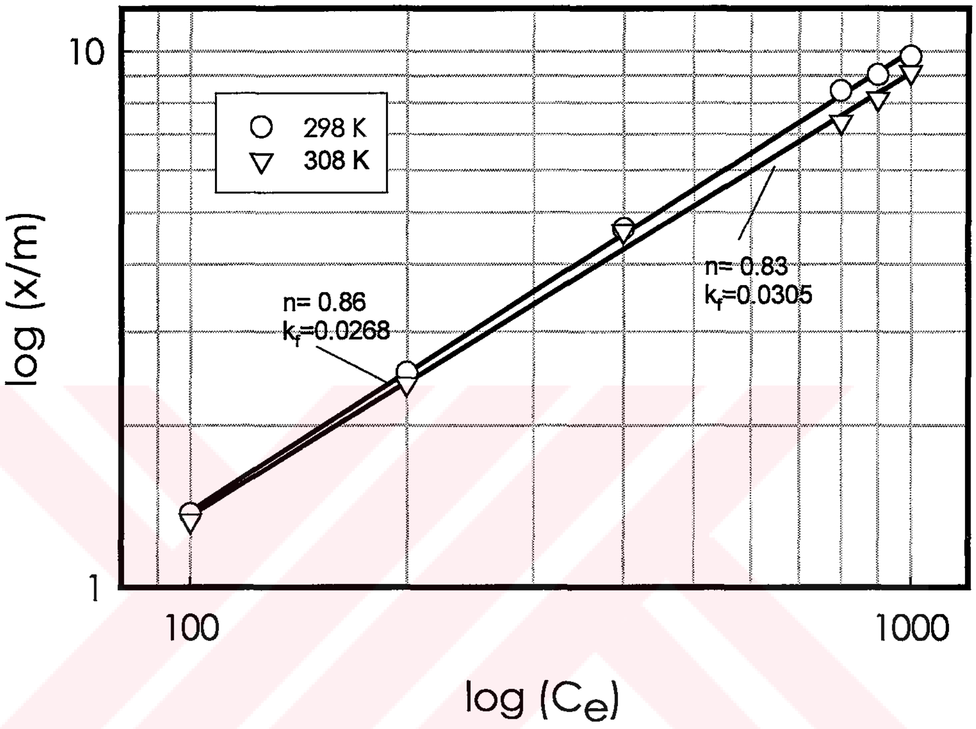

Figure 4.12. Applicability of Freundlich isotherms for Soma Lignite (S/L=0.05, pH: Natural)

Langmuir Isotherm

The langmuir adsorption isotherm is defined as

$$(x/m)= (ak_L C_e) / (1+k_L C_e) \qquad (4.2)$$

where; x/m : amount adsorbate adsorbed per unit weight of adsorbent.

C_e : equilibrium concentration of adsorbate in solution after adsorption

a : empirical Langmuir constant which represents maximum adsorption capacity (mg/g)

k_L : empirical Langmuir constant (l/mg) (Finqueneisel G. *et. al,* 1998)

Assuming the above equation (Eq. 4.2) as (Eq. 4.3)

$$C_e/[(x/m)]=[(1/ak_L)+(1/a)C_e \qquad (4.3)$$

and plotting of $C_e/(x/m)$ vs C_e give a straight line with slope $1/a$ and intercept $1/ak$. In this equation, a is the amount adsorbed per gram of adsorbent, corresponding to complete coverage (Abburi, K., 2003). It was calculated as 33.33 and 25.0 at 298 and 308 K, respectively. k_L is the Langmuir constant (L/g), which is an energy constant, indicating the adsorptivity of the solute.

The data in Figure 4.12 for S/L = 0.05 at neutral pH for Soma lignite is plotted again in Figure 4.13 to test the applicability of Langmuir isotherm. It can be seen that, the fit is not as good as that obtained with the Freundlich isotherm. The a and k_L values for this data are 33.3; $4.16.10^{-4}$ for 298 K and 25.0; $5.5.10^{-4}$ for 308 K, respectively. If we take the avarage a value of about 29 for the two data sets, it means that, assuming monolayer coverage, 29 mg phenol would be adsorbed per gram of lignite surface at complete surface covarage. This is the main premise of the Langmuir model. Hovewer, if we make a small calculation, we find that 29 mg phenol (molecular weight of 94.144 g/mol ; parking area of 30.5 A^0) would require a surface area of about 56.6 m^2 per gram of lignite (assuming of course monolayer coverage) based on the data given in Figure 4.13. However, we know that, the avarage surface area of 1 gram of the Soma lignite sample was about 6.1 m^2. Hence, the data show that, phenol must be adsorbing in multilayers. Then, it is not surprising that the Langmuir isotherm does not represent our data well.

If we refer to the discussion in Figure 4.7. where we found that 60 % of the Soma lignite surface was available for adsorption, we could see that, this 60 % value is a maximum, since it was calculated based on monolayer adsorption and should be much smaller in the case of multilayer adsorption case. This simply says that, most of the lignite surface does not contribute to phenol adsorption.

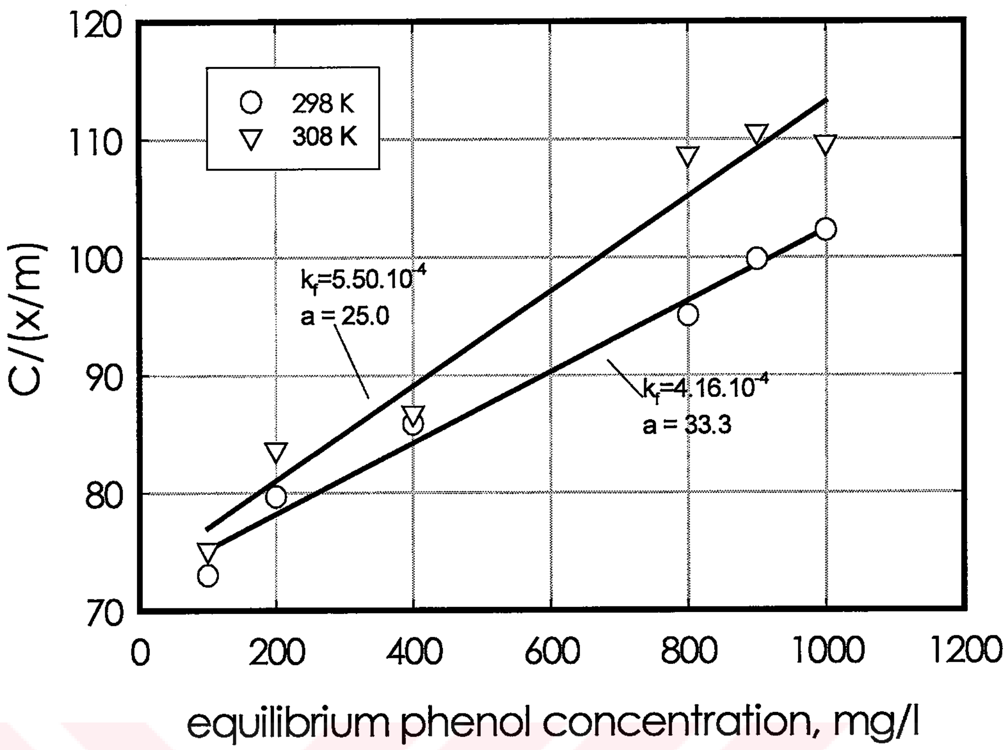

Figure 4.13. Applicability of Langmuir isotherms for phenol adsorption on Soma Lignite (S/L=0.05, pH; Natural)

Table 4.3. Comperasion of Freundlich and Langmuir Parameters of the System

Freundlich Parameters			
Temperature	n	k_f	r^2
298 K	0.86	0.0268	0.9995
308 K	0.83	0.0305	0.9996

Langmuir Parameters				
Temperature	k_L	a	k_l x a	r^2
298 K	$4.16.10^{-4}$	33.3	0.0139	0.9832
308 K	$5.50.10^{-4}$	25.0	0.0138	0.9653

4.3.2. Activation Energy of the Adsorption Process

The data in Figure 4.11 was replotted in the form of log C versus t (time) where C is the residual phenol concentration in solution (Figure 4.14).

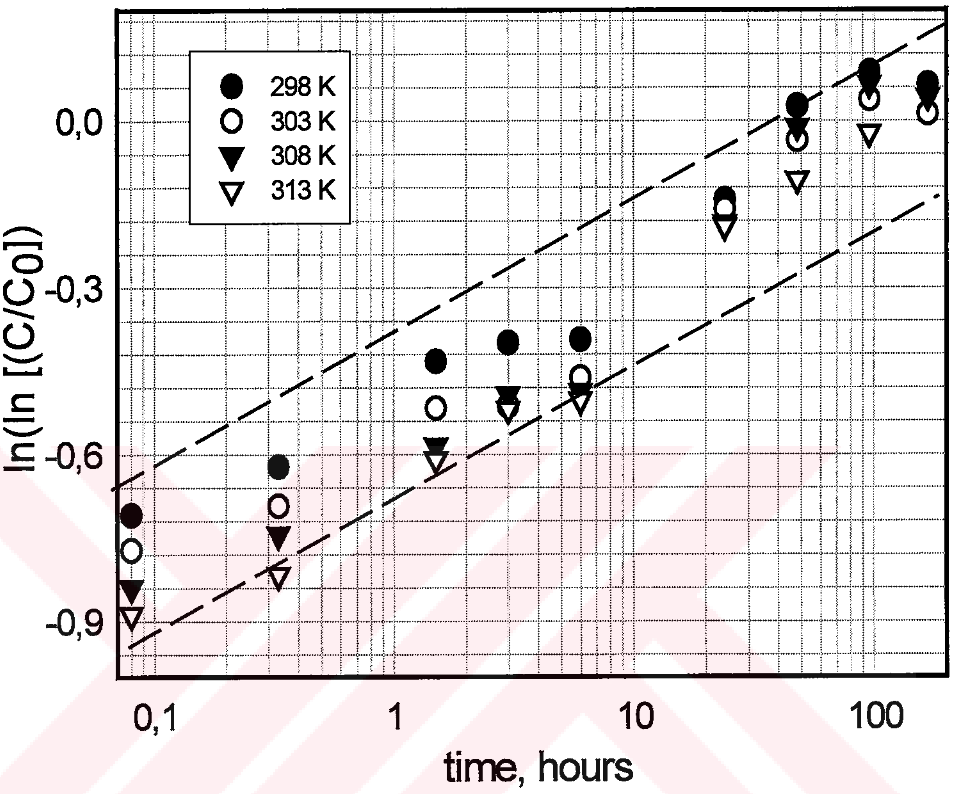

Figure 4.14. Applicability of Arrhenious Equation to the phenol adsorption on Soma Lignite

Since a first order reaction is given as

$$C = C_0 \exp(-kt) \tag{4.4}$$

$$log\ C = log\ C_o - kt \tag{4.5}$$

$$log\ log\ C/C_o = log\ k + log\ t \tag{4.6}$$

found a plot of *log C* versus *t*, (or log (log C/C_o) versus log *t* should yield a stright line mathematically. Figure 4.14 indicates that, adsorption of phenol on Soma coal is governed by a first order reaction. (Yin G. *et al,* 2002, Rengeraj S. *et al* 2001 and Atkins P.V., 1994)

hence, adsorption capacity is

$$q_t = q_e[1 - \exp(-kt)] \qquad (4.7)$$

where t is the contact time at different temperatures in terms of min, C_0 and C refers to starting and time dependent concentration of phenol, respectively, in terms of mg/L. q_t and q_e stand for the time dependent adsorption capacity and adsorption capacity at equilibrium in terms of mg phenol/g coal. k $\mathrm{min}^{-1}$is the apperent reaction constant.

The apparent reaction constant at different temperatures are thus calculated according to Eq. 4.4 and listed in Table 4.4.

Table 4.4. Apparent Reaction Rate Constant at Different Temperatures.

	298K	303K	308K	313K
k (min^{-1})	0.1454	0.1578	0.1659	0.1786

Arrhenious equation which relates the apparent rate constant with the reaction temperature is given as

$$ln\, k = ln\, A - (E_a / RT) \qquad (4.8)$$

here, A is the pre-exponential factor or frequency factor which can be calculated as exp(intercept) and E_a is the activation energy and can be directly calculated from the slope of the ln k versus 1/T plot. The data in Table 4.4 was plotted in this form in Figure 4.15 and E_a value calculated from the slope is -10.325 kJ.

$$k = 9.45\ exp\left(\frac{-10325}{RT}\right) \qquad (4.9)$$

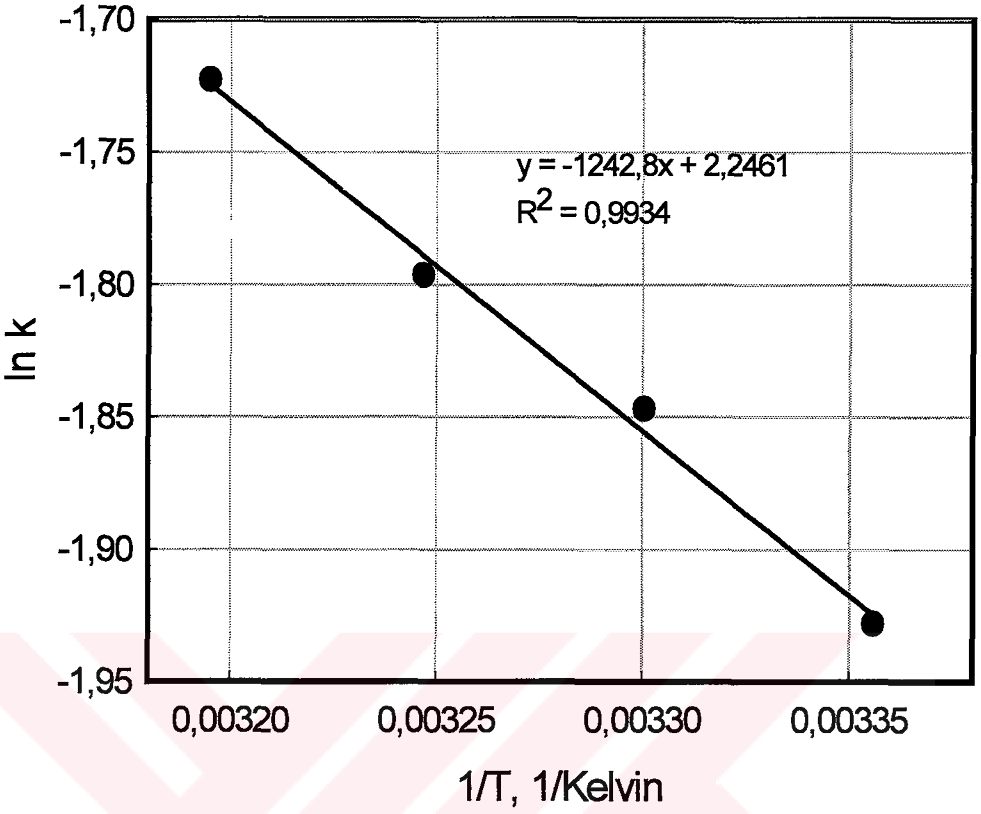

Figure 4.15. Linear regration of 1/T vs ln k calculated from Arrhenius Equation.

Thus the apparent activation energy, Ea, for the adsorption of phenol on Soma coal is much less than 40 kJ/mol, indicating that the adsorption of phenol on coal surface falls into the category of physical adsorption process.. (Atkins P.V., 1994 and Ying G. *et. al,* 2001)

4.3.3. Heat of Adsorption

The heat of adsorption was calculated by applying the Van't Hoff equation to the adsorption isotherm at 298 and 308 K Eq.(4.9). Detail of calculations can be found in Appendix H3.

$$\Delta H = \frac{RT_1T_2\ln(K_2/K_1)}{T_2 - T_1} \qquad (4.10)$$

$K_{1,2}$ = (mg/g)/(mg/L)

where K_1 and K_2 stand for phenol equilibrium concentration rate at T_1 and T_2, corresponding to adsorption capacity . The heat of adsorption as a function of adsorption capacity is shown in Figure 4.16. It is seen that the heat of adsorption increases with an increase in adsorption capacity. When the phenol amount adsorbed was around 3 mg, the heat of adsorption nearly negligible. This exothermic adsorption system has the maximum entalphy of -20.29 kJ/mol when the 7.89 mg phenol adsorbed on coal. This is the indication of physical adsorption mechanim, because it takes much less adsorption heat in contrast to chemical adsorption, and dispersion forces act a major role in the process. A decrease in the adsorbed amount of phenol on coal surface with an increase in temperature is also another indication of physical adsorption (Suzuki, M., 1990).

Gibbs Free Energy of the adsorption system was calculated accoding to Eq. 4.7. as kJ/mol.

$$\Delta G = [\, R.T_{1,2}.\ ln(K_{1,2}) \,]/1000 \qquad (4.11)$$

Gibbs Free Energy of phenol adsorption on Soma coal changed between -6.45 and -9.42 kJ/mol, and entropy changed between -42.23 and 9.50 J/mol K. These ranges were an other indication of physical adsorption of phenol on coal (Atkins, P.V., 1994). Entalphy (ΔH), free energy (ΔG) and entropy (ΔS) of the system are tabulated in Table 4.5.

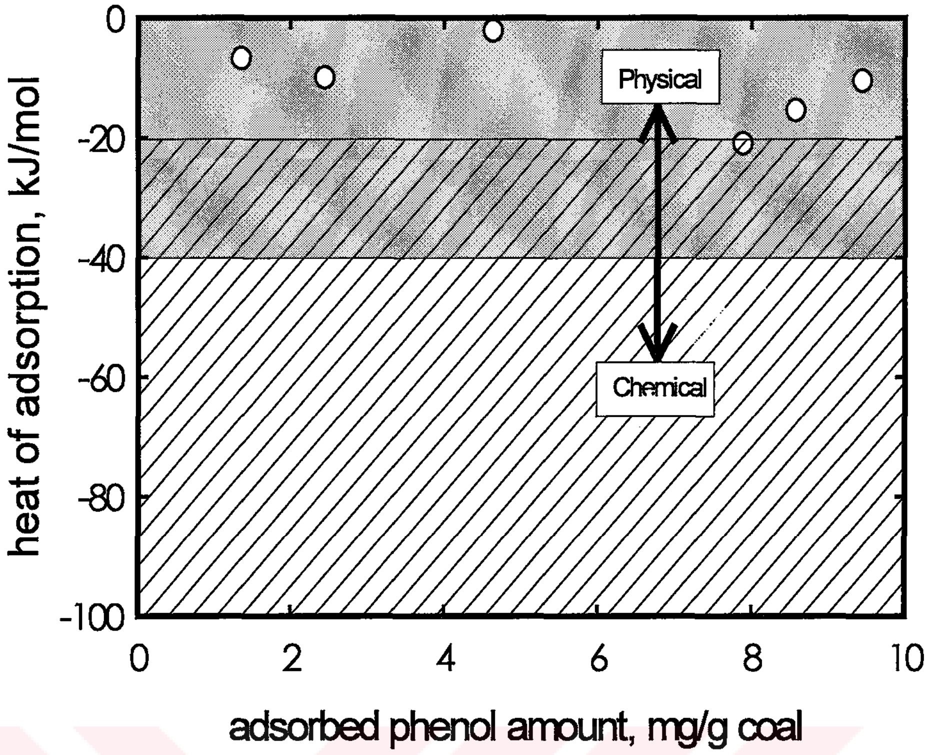

Figure 4.16. Change of enthalpy for phenol adsorption process on Soma Lignite.

Table 4.5. Enthalpy and Gibbs Free Energy of Phenol Adsorption on Soma Lignite.

Adsorbed phenol amount (mg/g)	**ΔH (kJ/mol)** **-R xT x ln K****	**ΔG (kJ/mol)** **ΔH - T ΔS**
1.35	-6.54	-9.42
2.08	-6.59	-7.88
4.63	-2.11	-8.35
7.89	-20.29	-7.50
8.58	-14.93	-7.32
9.29	-10.15	-7.27
9.08	-9.61	-6.45
Chemisorption: -ΔH > 40 kJ/mol, + ΔH > 200kJ/mol *Physiorption: -ΔH < 25 kJ/mol*		

4.4. Discussion on the Phenol Adorption Mechanism

The results given above suggest that only a fraction of the lignite surface is available for adsorption conrtributes to the removal. The reasons for this could be several. The lignite samples used in this study are heterogeneous substances consisting of ash-forming minerals and organic matter (see Chapter III). These low rank coals are expected to contain large amounts of polar groups such as –OH, -COO, -O, -N, and –S and exhibit mostly polar (hydrophilic) behaviour. Hence, the contribution of mineral matter or the polar groups, or the aliphatic-aromatic non-polar part of the coal, on the adsorption is not clear. In the literature, the phenol adsorption on pure carbons was determined by the so-called $\pi-\pi$ interactions (dispersion forces between phenol π electrons ring and π electrons of carbons) and "donor-acceptor complex" formation between the surface carbonyl groups (electron donors) and the aromatic ring of phenol acting as the acceptor (Terzyk A.P., 2003, Redovic L.R. *et al.,* 2001 and Coughlin *et. al,* 1968). However "solvent effect" was suggested to form the boundry between the $\pi-\pi$ interactions and "donor-acceptor complex" formation. They found a linear correlation between the average (300-320K) adsorbability of phenol calculated for the studied carbons and the total concentration of surface bases and carboxyls at infinite dilutions. The most acidic, carboxyls, and some of the most basic groups decreased phenol adsorption at small concentrations. At acidic pH, the more polar the surface of carbon, the lower the adsorbability of phenol. The effect of the chemical composition of surface layer was the largest at the lowest temperature studied (at 300K). According to Tessmer et al., (1997) the adsorptive capacity and the amount of irreversible adsorption was found to increase significantly in the presence of dissolved oxygen (oxic conditions) due to the oligomerization of these compounds through oxidative coupling reactions. However, the effect of oxidation was suggested to effect the adsorption depending on phenol concentration (Terzyk A.P.*et. al,* 2003).

The literature also suggests physical adsorption of the non-polar aromatic phenol onto various substrates such as silica gel and zeolites besides activated carbon (Roostaci N. *et. al,* 2004 and Shen Y. *et. al,* 2002). Our studies on the calculation of activation energy and the heat of adsorption, which was discussed in the previous paragraphs, support the findings that the adsorption of phenol on this lignitic coal was also through physical interactions (Yin G. *et. al,* 2002 and Atkins W.,1994).

Desorption of phenol from coal in water was also tested to support the adsorption mechanism as physical and the results presented in Figure 4.17 and 4.18 for Soma and Yatağan coal, respectively. It is seen from the figures that desorption of phenol in water is almost 33.22 % for Soma and 43.20 % for Yatagan coals without any chemical treatment method (adding phenol contaminated coals into the pure water).

These results suggest the possibility of irreversible adsorption for soma and Yatağan lignitic coal surface sites. However, as it is pointed out earlier, the surface structure of lignite is quite complex and further research is required to explain the contributions of different surface sites on the irreversible and reversible adsorption of phenol. The degree and type of this contribution might also depend on solvent chemistry.

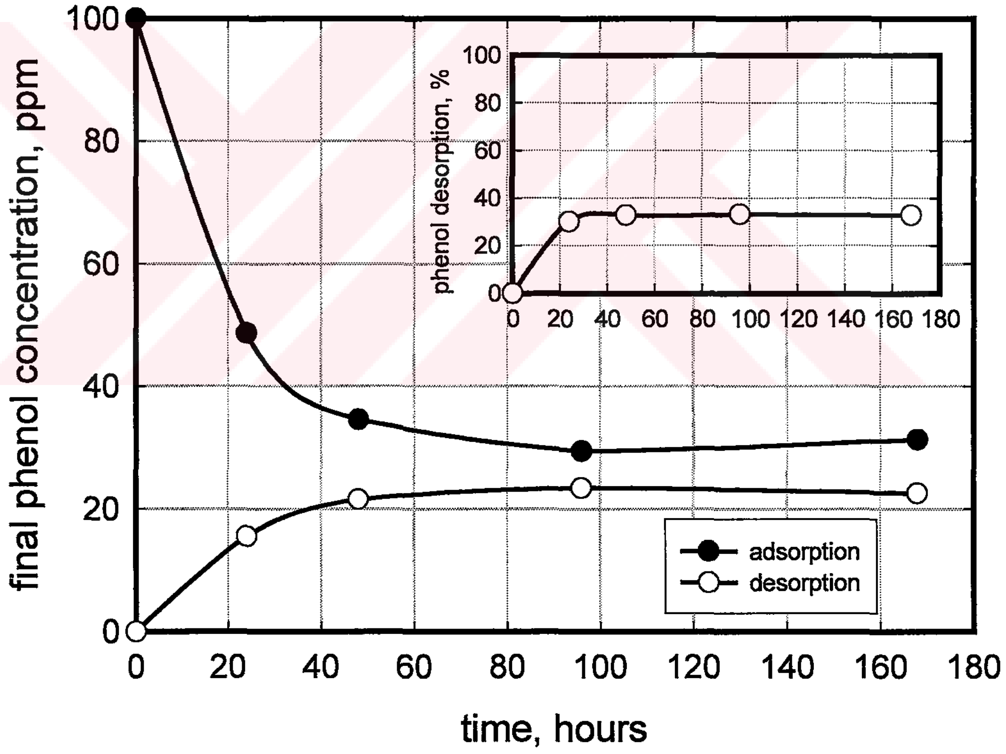

Figure 4.17. Adsorption-desorption curves of phenol on Soma coal (S/L=0.05, pH: natural, Temperature: 298 K)

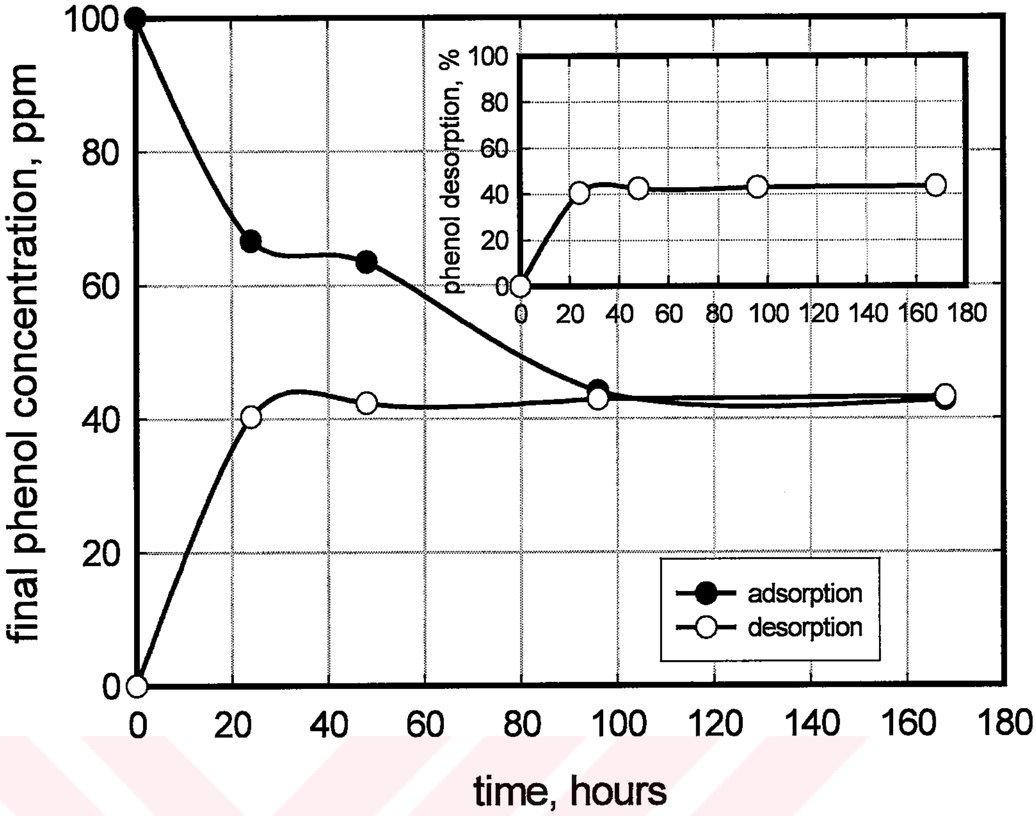

Figure 4.18. Adsorption-desorption curves of phenol on Yatagan coal (S/L=0.05, pH : natural, Temperature: 298 K)

4.5. Water Quality After Phenol Adsorption: Leaching of Coal

It is important to control water quality with respect to organic and inorganic compounds after phenol adsorption. Determination method of organics (Soxhlet evaporator-condenser set-up) were explained in chapter III. By this method, it was found that the total amount dissolved was 1.57 mg for 1 g of Soma lignitic coal. Out of this amount 0.76 mg was comprised of such metals as Ca, Mg, Na and K as will be given in the following paragraphs. Hence, the total amount of organic matter which dissolved from the coal, most probably as humic species, was in the order of 0.81 mg for each gram of coal. For Yatağan lignitic coal, the total amount dissolved was 1,02 mg for 1 g of coal. 0.23 mg metals for Yatağan coal were detected in water. As a result, 0.79 mg humic species for 1 g of Yatağan coal dissolved to water. Therefore, it can be said that dissolution of organic substances is very low for these coals and can be neglected for further analysis.

The water quality with respect to heavy metals and major elements was determined using the Standard Method ASTM D-4793. The results are presented in Figure 4.19 and 4.20 for Soma and Yatagan linites repectively. It can be seen that most of the heavy metals do not dissolve at all and among the ones which show certain dissolution, none is above the limiting values set by the Environmental Regulations for Water Quality in Turkey for the water quality classes I, II, III and IV.

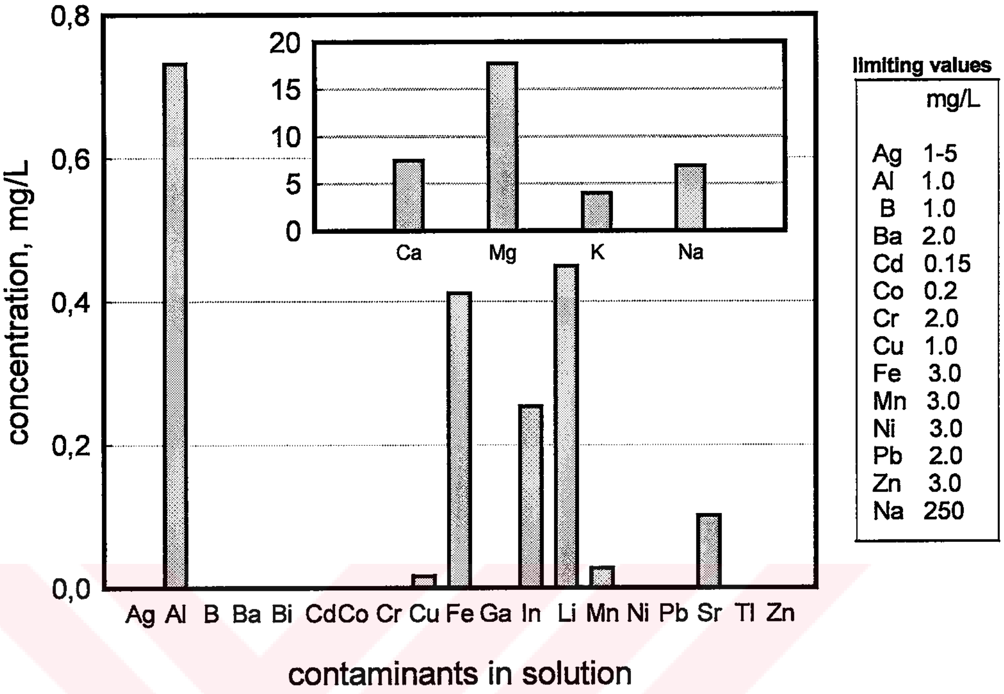

Figure 4.19. The results of the ASTM analyses for Soma lignite sample for major elements and heavy metals with limiting values set by the Environmental Regulations for Wastewater Quality in Turkey.

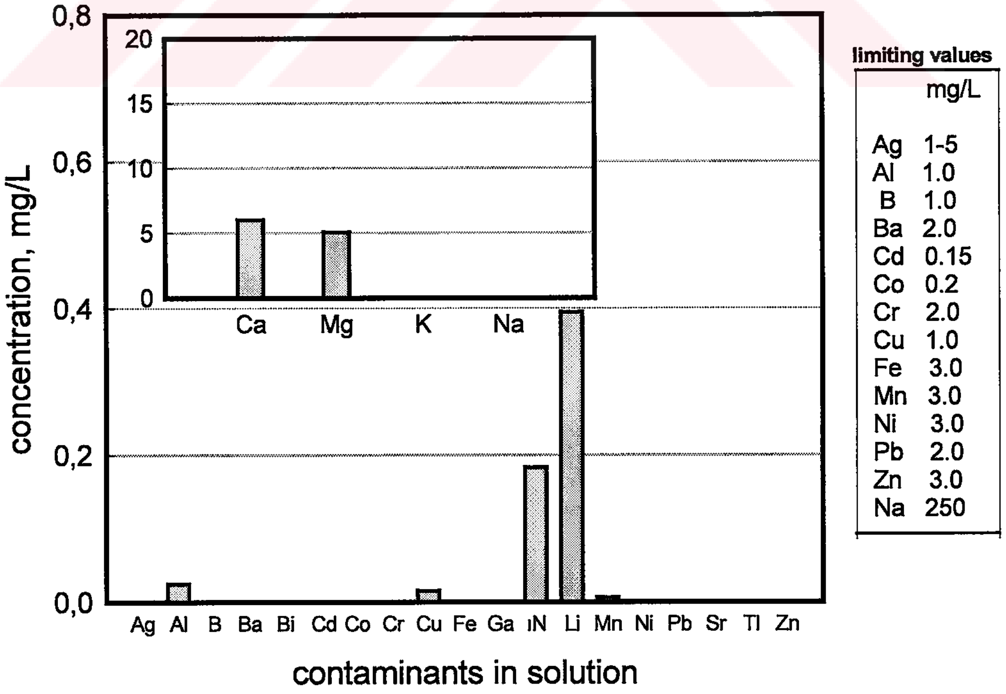

Figure 4.20. The results of the ASTM analyses for Yatagan lignite sample for major elements and heavy metals with limiting values set by the Environmental Regulations for Wastewater Quality in Turkey.

4.6. Effect of Heavy Metals Present in Water on Phenol Adsorption

Wastewaters also contain significant amounts of heavy metals. In order to have an idea about the effect of such contaminants on adsorption of phenol, studies were also carried out in the presence of heavy metals for Soma and Yatagan lignitic coals..

The starting water was prepared by addition of about 10 ppm of several compounds such as $HgCl_2$, $CrCl_3$, $Cu(NO_3)_2$, Co $(NO_3)_2$, $Zn(NO_3)_2$ $Pb(NO_3)_2$ and each compound was studied separately. Metal concentrations in solutions and their species at experiment pH (pH=8.0) were given in chapter 3 (Table 3.3). The results of these studies were presented as mg phenol/g coal and removal percent in Figures 4.21 and 4.22 for Soma, and Yatağan lignites respectively.

It is seen that their presence affect the phenol removal negatively depending on coal and element type. For example, in case of Soma coal, Hg and Co are the ones which affect the phenol adsorption the most by about 20%. However, their own concentration in water decrease to almost zero during the adsorption. Their effects can be ordered as Hg > Pb > Cu > Zn > Cr > Co and exact values of negative effects are 0.47, 0.43, 0.35, 0.31, 0.28 and 0.17 mg phenol/g coal for Soma coal.

However, this effect may not be mainly due to the competative adsorption, since their main receptive adsorption sites may be different on coal surface.

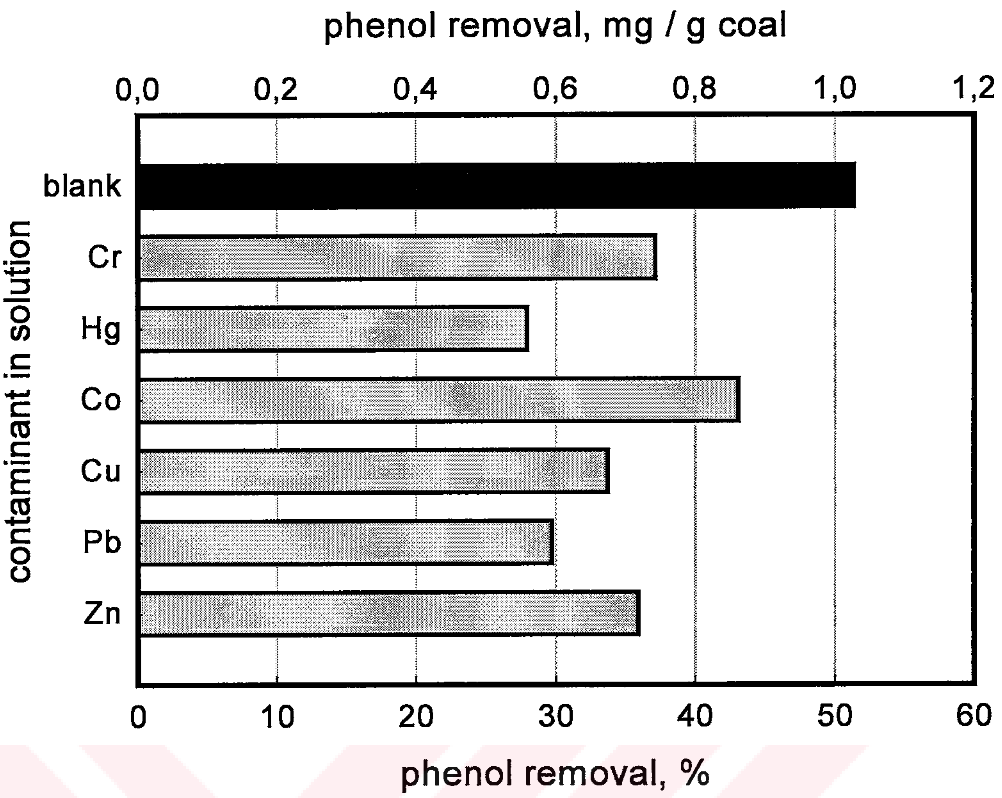

Figure 4.21. Removal of Phenol by Soma Lignite in the Presence of Heavy Metals and Salts. (S/L=0.05; pH:Natural; Contact time:24 hrs, Temperature: 298 K)

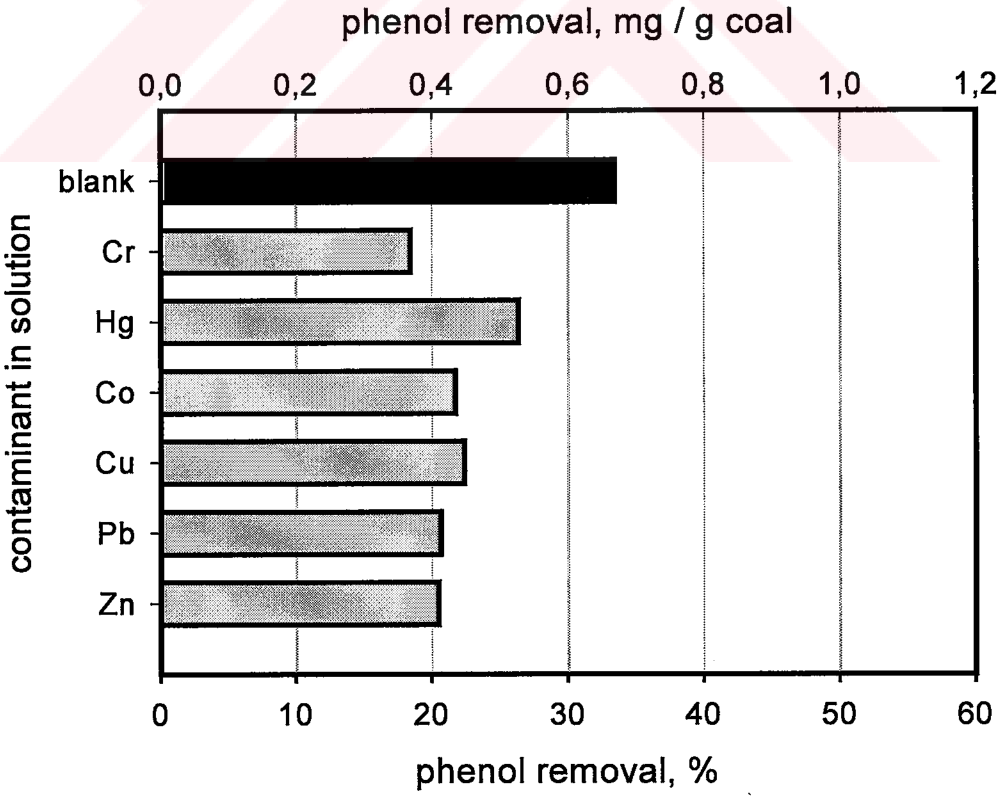

Figure 4.22. Removal of phenol by Yatağan Lignite in the Presence of Heavy Metals (S/L=0.05; pH:Natural; Contact time:24 hrs, Temperature: 298 K)

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Batch adsorption studies were conducted to investigate the adsorption capacity of Soma and Yatağan lignitic coals under different conditions such as S/L ratio, time and temperature. Based on the results of these studies and the activation energy interpreted from the adsorption data obtained as a function of temperature and the use of Arhenius equation, heat of adsorption from the Wan't Hoff equation, an adsorption mechanism for phenol was proposed and discussed. The specific conclusions were listed below.

1. Lignite coal is able to adsorb phenol upto 100% when sufficient surface area is provided for adsorption. At an S/L ratio of 0.1, the amount of phenol adsorbed was 90% after 96 hours for Soma coal. At the same S/L ratio, the adsorption capacity was around 63% after 6 hours. Experiments with different S/L ratios showed that when solid amount in solution increase, removal of phenol increase, but when little amounts of Soma coal were used, phenol adsorbed amount was much efficient than other cases.

2. It is proposed that, based on the maximum adsorption values on the time axis at various S/L ratios suggest that the fraction of available surface sites which is receptive to phenol for adsorption is around 60% for Soma coal and 43% for Yatagan coal. Studies are recommended to determine the contribution of various components such as mineral matter, acidic surface functional groups, aliphatic surface groups, etc., to the phenol adsorption.

3. Adsorption on lignite seems to be of physical origin as determined from the activation energy (10.3 kJ/mol) and the maximum heat of adsorption (-20.2 kJ/mol) calculations. The low magnitude of both energies suggests that adsorption of phenol on coal through physical bonding.

4. Freundlich Adsorption Model described the adsorption system well, with high efficiency and low affinity characteristics. The Langmuir Model did not describe the system as good as Freundlich Model since its main assumption of monolayer coverage. This indicates that, most of the lignite surface does not contribute to phenol adsorption.

5. Water quality following adsorption was within environmental standards as measured by the ASTM procedure. The concentration levels of major elements and heavy metals were all under the standard levels defined for waste water. The amount of organic matter dissolved from the coal was also negligible.

6. Heavy Metals and metal salts affected adsorption process negatively. This is because, heavy metals were adsorbed by coals and phenol could not find a large area on coal.

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APPENDIX A

EXPERIMENTAL RAW DATA

Table A.1. Phenol Adsorption on Soma Lignitic Coal at Various S/L Ratios and Time

$[C_0]$= 100 ppm, pH: natural, mixing speed 600 rpm, T=298 K

Sample: Soma Lignitic Coal
S/L: 0.0125

contact time (minute)	contact time (hours)	phenol removal (%)	final phenol concentration (mg/L)	adsorbed phenol amount (mg /kg coal)	adsorbed phenol amount (mol/kg coal)
5	0,08	3,95	96,05	316,00	0,003
20	0,33	5,69	94,31	455,20	0,005
90	1,50	9,95	90,05	796,00	0,008
180	3,00	10,29	89,71	823,20	0,009
360	6,00	10,29	89,71	823,20	0,009
1440	24,00	19,55	80,45	1564,00	0,017
2880	48,00	28,29	71,71	2263,20	0,024
5760	96,00	33,49	66,51	2679,20	0,028
10080	168,00	20,39	79,61	1631,20	0,017

S/L: 0.025

contact time (minute)	contact time (hours)	phenol removal (%)	final phenol concentration (mg/L)	adsorbed phenol amount (mg /kg coal)	adsorbed phenol amount (mol/kg coal)
5	0,08	12,22	87,78	488,80	0,005
20	0,33	14,15	85,85	566,00	0,006
90	1,50	17,29	82,71	691,60	0,007
180	3,00	16,82	83,18	672,80	0,007
360	6,00	18,89	81,11	755,60	0,008
1440	24,00	37,69	62,31	1507,60	0,016
2880	48,00	45,49	54,51	1819,60	0,019
5760	96,00	51,22	48,78	2048,80	0,022
10080	168,00	44,28	55,72	1771,20	0,019

S/L: 0.05

contact time (minute)	contact time (hours)	phenol removal (%)	final phenol concentration (mg/L)	adsorbed phenol amount (mg /kg coal)	adsorbed phenol amount (mol/ kg coal)
5	0,08	17.02	82,98	340,40	0,004
20	0,33	25.75	74,25	514,97	0,005
90	1,50	27.60	72,40	552,05	0,006
180	3,00	30.72	69,28	614,30	0,007
360	6,00	31.25	68,76	624,90	0,007
1440	24,00	53.76	46,24	1075,23	0,011
2880	48,00	64.89	35,11	1297,75	0,014
5760	96,00	72.90	27,10	1458,01	0,015
10080	168,00	69.00	31,00	1380,00	0,015

$[C_0]$= 100 ppm, pH: natural, mixing speed 600 rpm, T=298 K

Sample: Soma Lignitic Coal

S/L: 0.1

contact time (minute)	contact time (hours)	phenol removal (%)	final phenol concentration (mg/L)	adsorbed phenol amount (mg /kg coal)	adsorbed phenol amount (mol/kg coal)
5	0,08	33,29	66,71	332,90	0,004
20	0,33	47,56	52,44	475,60	0,005
90	1,50	53,19	46,81	531,90	0,006
180	3,00	61,12	38,88	611,20	0,006
360	6,00	63,30	36,70	633,00	0,007
1440	24,00	75,00	25,00	750,00	0,008
2880	48,00	82,00	18,00	820,00	0,009
5760	96,00	88,48	11,52	884,80	0,009
10080	168,00	88,54	11,46	885,40	0,009

S/L: 0.2

contact time (minute)	contact time (hours)	phenol removal (%)	final phenol concentration (mg/L)	adsorbed phenol amount (mg /kg coal)	adsorbed phenol amount (mol/kg coal)
5	0,08	62,35	37,65	311,75	0,003
20	0,33	70,21	29,79	351,05	0,004
90	1,50	74,63	25,37	373,15	0,004
180	3,00	82,27	17,73	411,35	0,004
360	6,00	84,88	15,12	424,40	0,005
1440	24,00	90,88	9,12	454,40	0,005
2880	48,00	95,35	4,65	476,75	0,005
5760	96,00	97,95	2,05	489,75	0,005
10080	168,00	97,92	2,08	489,60	0,005

S/L: 0.4

contact time (minute)	contact time (hours)	phenol removal (%)	final phenol concentration (mg/L)	adsorbed phenol amount (mg /kg coal)	adsorbed phenol amount (mol/kg coal)
5	0,08	88,65	11,35	221,63	0,002
20	0,33	89,47	10,53	223,68	0,002
90	1,50	89,84	10,16	224,60	0,002
180	3,00	90,23	9,77	225,58	0,002
360	6,00	92,96	7,04	232,40	0,002
1440	24,00	96,10	3,90	240,25	0,003
2880	48,00	97,94	2,06	244,85	0,003
5760	96,00	98,69	1,31	246,73	0,003
10080	168,00	99,03	0,97	247,58	0,003

Table A.2. Phenol Adsorption on Yatağan Lignitic Coal at Various S/L Ratios and Time

[C_o]= 100 ppm, pH: natural, mixing speed 600 rpm, T=298 K

Sample: Yatağan Lignitic Coal

S/L: 0.0125

contact time (minute)	contact time (hours)	phenol removal (%)	final phenol concentration (mg/L)	adsorbed phenol amount (mg /kg coal)	adsorbed phenol amount (mol/kg coal)
5	0,08	9,02	90,98	721,60	0,008
20	0,33	8,15	91,85	652,00	0,007
90	1,50	8,89	91,11	711,20	0,008
180	3,00	7,42	92,58	593,60	0,006
360	6,00	8,49	91,51	679,20	0,007
1440	24,00	5,02	94,98	401,60	0,004
2880	48,00	8,35	91,65	668,00	0,007
5760	96,00	15,49	84,51	1239,20	0,013
10080	168	15,33	84,67	1226,40	0,013

S/L: 0.025

contact time (minute)	contact time (hours)	phenol removal (%)	final phenol concentration (mg/L)	adsorbed phenol amount (mg /kg coal)	adsorbed phenol amount (mol/kg coal)
5	0,08	12,29	87,71	491,60	0,005
20	0,33	12,42	87,58	496,80	0,005
90	1,50	10,89	89,11	435,60	0,005
180	3,00	11,55	88,45	462,00	0,005
360	6,00	12,09	87,91	483,60	0,005
1440	24,00	10,29	89,71	411,60	0,004
2880	48,00	19,35	80,65	774,00	0,008
5760	96,00	30,89	69,11	1235,60	0,013
10080	168	29,84	70,16	1193,60	0,013

S/L: 0.05

contact time (minute)	contact time (hours)	phenol removal (%)	final phenol concentration (mg/L)	adsorbed phenol amount (mg /kg coal)	adsorbed phenol amount (mol/kg coal)
5	0,08	19,42	80,58	388,40	0,004
20	0,33	21,62	78,38	432,40	0,005
90	1,50	23,62	76,38	472,40	0,005
180	3,00	17,69	82,31	353,80	0,004
360	6,00	19,09	80,91	381,80	0,004
1440	24,00	33,42	66,58	668,40	0,007
2880	48,00	36,62	63,38	732,40	0,008
5760	96,00	56,02	43,98	1120,40	0,012
10080	168,00	55,87	44,13	1117,40	0,012

$[C_0]$= 100 ppm, pH: natural, mixing speed 600 rpm, T=298 K

Sample: Yatağan Lignitic Coal
S/L : 0.1

contact time (minute)	contact time (hours)	phenol removal (%)	final phenol concentration (mg/L)	adsorbed phenol amount (mg /kg coal)	adsorbed phenol amount (mol/kg coal)
5	0,08	29,65	70,35	296,50	0,003
20	0,33	32,24	67,76	322,40	0,003
90	1,50	33,48	66,52	334,80	0,004
180	3,00	35,66	64,34	356,60	0,004
360	6,00	37,64	62,36	376,40	0,004
1440	24,00	57,00	43,00	570,00	0,006
2880	48,00	75,00	25,00	750,00	0,008
5760	96,00	90,67	9,33	906,70	0,010
10080	168,00	89,16	10,84	891,60	0,009

S/L: 0.2

contact time (minute)	contact time (hours)	phenol removal (%)	final phenol concentration (mg/L)	adsorbed phenol amount (mg /kg coal)	adsorbed phenol amount (mol/kg coal)
5	0,08	38,76	61,24	193,80	0,002
20	0,33	42,59	57,41	212,95	0,002
90	1,50	44,21	55,79	221,05	0,002
180	3,00	44,86	55,14	224,30	0,002
360	6,00	45,07	54,93	225,35	0,002
1440	24,00	69,37	30,63	346,85	0,004
2880	48,00	96,00	4,00	480,00	0,005
5760	96,00	98,56	1,44	492,80	0,005
10080	168,00	98,48	1,52	492,40	0,005

S/L: 0.4

contact time (minute)	contact time (hours)	phenol removal (%)	final phenol concentration (mg/L)	adsorbed phenol amount (mg /kg coal)	adsorbed phenol amount (mol/kg coal)
5	0,08	51,23	48,77	128,08	0,001
20	0,33	57,49	42,51	143,73	0,002
90	1,50	66,98	33,02	167,45	0,002
180	3,00	67,02	32,98	167,55	0,002
360	6,00	68,16	31,84	170,40	0,002
1440	24,00	86,02	13,98	215,05	0,002
2880	48,00	99,02	0,98	247,55	0,003
5760	96,00	99,04	0,96	247,60	0,003
10080	168,00	99,04	0,96	247,60	0,003

Table A.3. Phenol Adsorption on Soma Lignitic Coal at Various Temperatures

Soma Lignite S/L: 0.05 Temperature: 298 K C_0=100 mg/L

contact time (minute)	**contact time (hours)**	**phenol removal (%)**	**final phenol concentration (mg/L)**	**adsorbed phenol amount (mg /kg coal)**	**adsorbed phenol amount (mol/kg coal)**
5	0,08	17,75	82,25	355,00	0,004
20	0,33	21,22	78,78	424,40	0,005
90	1,5	30,88	69,12	617,60	0,007
180	3	32,88	67,12	657,60	0,007
360	6	33,22	66,78	664,40	0,007
1440	24	51,35	48,65	1027,00	0,011
2880	48	65,42	34,58	1308,40	0,014
5760	96	70,55	29,45	1411,00	0,015
10080	168	68,69	31,31	1373,80	0,015

Soma Lignite S/L: 0.05 Temperature: 303 K C_0=100 mg/L

contact time (minute)	**contact time (hours)**	**phenol removal (%)**	**final phenol concentration (mg/L)**	**adsorbed phenol amount (mg /kg coal)**	**adsorbed phenol amount (mol/kg coal)**
5	0,08	15,55	84,45	311,00	0,003
20	0,33	18,35	80,65	387,00	0,004
90	1,5	26,22	73,78	524,40	0,006
180	3	26,42	73,58	528,40	0,006
360	6	29,15	70,85	583,00	0,006
1440	24	49,95	50,05	999,00	0,011
2880	48	60,23	39,77	1204,60	0,013
5760	96	66,62	33,38	1332,40	0,014
10080	168	64,21	35,79	1284,20	0,014

Soma Lignite S/L: 0.05 Temperature: 308 K C_0=100 mg/L

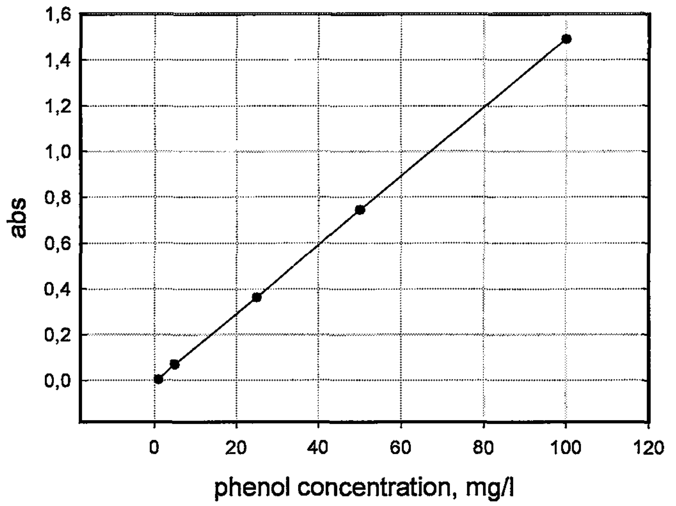
contact time (minute)	**contact time (hours)**	**phenol removal (%)**	**final phenol concentration (mg/L)**	**adsorbed phenol amount (mg /kg coal)**	**adsorbed phenol amount (mol/kg coal)**
5	0,08	13,49	87,85	0,243	0,003
20	0,33	16,50	82,85	0,343	0,004
90	1,5	22,89	78,11	0,4378	0,005
180	3	27,49	72,51	0,5498	0,006
360	6	27,75	72,25	0,555	0,006
1440	24	47,95	52,46	0,9508	0,010
2880	48	62,25	37,75	1,245	0,013
5760	96	68,69	31,31	1,3738	0,015
10080	168	66,81	33,19	1336,2	0,014

Soma Lignite S/L: 0.05 Temperature: 313 K C_0=100 mg/L

contact time (minute)	**contact time (hours)**	**phenol removal (%)**	**final phenol concentration (mg/L)**	**adsorbed phenol amount (mg /kg coal)**	**adsorbed phenol amount (mol/kg coal)**
5	0,08	12,15	86,51	0,2698	0,003
20	0,33	14,15	85,85	0,283	0,003
90	1,5	21,79	77,11	0,4578	0,005
180	3	26,09	73,91	0,5218	0,006
360	6	26,95	73,05	0,539	0,006
1440	24	47,54	52,05	0,959	0,010
2880	48	54,27	45,73	1,0854	0,012
5760	96	61,25	38,75	1,225	0,013

APPENDIX B

SAMPLE CALCULATIONS



phenol conc. mg/L (X)	Abs (Y)
1	0.0036
5	0.07
25	0.362
50	0.745
100	1.489

Y= 0.015X - 0.0087

Correl: 0.999980769

An example for calculation of phenol concentration
Sample: Soma Lignite with S/L ratio of 0.05
Phenol solution volume (V) : 100 ml
Initial phenol concentration (C_i): 100 g/mol
Molecular weight of phenol: 94.144 mg/mmol
Mixing time: 96 hours
Mixing speed: 600 rpm
Absorbance (abs) @ 270 nm wavelength : 0.4615

Phenol in solution as the unit of mg /l after batch experiment

$X = (Y + 0.0087) / 0.015$
$X = (0.4615 + 0.0087) / 0.015$
$X = 29.4503$

Penol removal

Removal rate = $(C_i - C_f^*) / 100$
Removal rate = $(100 - 29.4503) / 100$
Removal rate = 0.705497 (removal % = 70.55)

C_f : final phenol concentration in solution

Adsorbed Amount

Phenol amount in solution = 10 mg / 100 ml = 0.1 mg / ml
Coal amount in solution = 5 g / 100 ml =0.05 g / ml
Phenol amount / coal amount = 2 mg/g (when the removal % is equal to 100)
Adsorbed amount = $[((C_i - C_f))/100]*2$ mg / g
Adsorbed amount = 1.4110 mg phenol / g coal
Adsorbed amount = 1.4110 (mg/g) / 94.144 (mg/mmol)
Adsorbed amount = 0.015 mmol phenol /g coal

APPENDIX C

ZETA POTENTIAL MEASUREMENTS DATA

Table C.1. Zeta Potential Distribution of Soma Coal

Zeta potential (mV)	Intensity (Soma Lignite)			
	1st measurement	2nd measurement	3rd measurement	avarage
-47,6	0,000	0,000	0,000	0,000
-41,3	0,000	0,000	0,000	0,000
-34,9	0,000	0,000	0,000	0,000
-28,6	0,000	0,000	0,000	0,000
-22,2	14,500	3,300	4,400	7,400
-15,9	41,700	43,000	29,800	38,167
-9,5	43,800	48,800	48,700	47,100
-3,2	0,000	4,900	17,000	7,300
3,2	0,000	0,000	0,000	0,000
9,5	0,000	0,000	0,000	0,000
15,9	0,000	0,000	0,000	0,000
22,2	0,000	0,000	0,000	0,000
28,6	0,000	0,000	0,000	0,000
34,9	0,000	0,000	0,000	0,000
41,3	0,000	0,000	0,000	0,000
47,6	0,000	0,000	0,000	0,000

Table C.2. Zeta Potential Distribution of Yatağan Coal

Zeta potential (mV)	Intensity (Yatağan Lignite)			
	1st measurement	2nd measurement	3rd measurement	avarage
-47,6	0,000	0,000	0,000	0,000
-41,3	0,000	0,000	0,000	0,000
-34,9	0,000	0,000	0,000	0,000
-28,6	0,000	0,000	0,000	0,000
-22,2	30,500	38,130	26,500	31,710
-15,9	45,100	50,800	45,100	47,000
-9,5	24,400	10,800	28,500	21,233
-3,2	0,000	0,000	0,000	0,000
3,2	0,000	0,000	0,000	0,000
9,5	0,000	0,000	0,000	0,000
15,9	0,000	0,000	0,000	0,000
22,2	0,000	0,000	0,000	0,000
28,6	0,000	0,000	0,000	0,000
34,9	0,000	0,000	0,000	0,000
41,3	0,000	0,000	0,000	0,000
47,6	0,000	0,000	0,000	0,000

APPENDIX D

FREUNDLICH MODEL FOR PHENOL ADSORPTION ON SOMA LIGNITE

Table D.1. Calculation of Freundlich Model for Soma Coal

initial phenol (mg/l)	mg phenol/g coal @ 298 K				NEW (freundlich)
[C]	x/m	log [C]	log(x/m)		x/m
100,00	1,37	2,0000	0,1379		1,31
200,00	2,51	2,3010	0,3373		2,41
400,00	4,66	2,6021	0,6684		4,44
800,00	8,42	2,9031	0,9253		8,17
900,00	9,02	2,9542	0,9550		9,07
1000,00	9,78	3,0000	0,9903		9,95
1200,00	9,77	3,0792	0,9900		11,69
log(x/m)= logk+ n log[C]		SLOPE	0,8572	n=	0,86
		INTERCEPT	-1,58	k=	0,0268
$x/m=k[C]^n$		CORREL	0,9997		
initial phenol (mg/l)	mg phenol/g coal @ 308 K				NEW (freundlich)
[C]	x/m	log [C]	log(x/m)		x/m
100,00	1,33	2,0000	0,1246		1,29
200,00	2,39	2,3010	0,3197		2,31
400,00	4,61	2,6021	0,6633		4,16
800,00	7,36	2,9031	0,8668		7,50
900,00	8,14	2,9542	0,9105		8,28
1000,00	9,12	3,0000	0,9598		9,06
1200,00	9,05	3,0792	0,9568		10,57
log(x/m)= logk+ n log[C]		SLOPE	0,83	n=	0,83
		INTERCEPT	-1,53	k=	0,0305
$x/m=k[C]^n$		CORREL	0,9996		

APPENDIX E
HEAT OF ADSORPTION AND LANGMUIR MODEL

Table E.1. Calculation Method for Heat of Adsorption

mg/l	mg/l	mg /g	mg/l	mg /g	ml/g	ml/g			
[c]initial	[C]liquid (298K)	[q]solid (298K)	[C]liquid (308K)	[q]solid (308K)	K_1 (T=298K)	K_2 (T= 308K)	K_2 / K_1	ln [(K_2)/(K_1)]	ΔH (kJ/mol)
100	31,32	1,37	33,19	1,34	43,857	40,255	0,9179	-0,086	-6,54
200	91,30	2,17	95,60	2,09	23,812	21,843	0,9173	-0,086	-6,59
400	167,01	4,66	169,71	4,61	27,901	27,139	0,9727	-0,028	-2,11
800	379,00	8,42	432,10	7,36	22,216	17,028	0,7665	-0,266	-20,29
900	449,24	9,02	493,14	8,14	20,068	16,501	0,8223	-0,196	-14,93
1000	511,05	9,78	544,20	9,12	19,135	16,751	0,8754	-0,133	-10,15
1200	711,38	9,77	747,38	9,05	13,737	12,112	0,8817	-0,126	-9,61

$$\Delta H = \frac{RT_1T_2 \ln(K_2 / K_1)}{T_2 - T_1}$$

Table E.2. Calculation Method for Langmuir Model

initial phenol (mg/l)	mg phenol/g coal @298 K				NEW (Langmuir)	
[C]	x/m		[C] / (x/m)		x/m	
100,00	1,37		72,7907992		1,4614362	
	2,51					
400,00	4,66		85,8404541		5,8457447	
800,00	8,42		95,0118765		11,691489	
900,00	9,02		99,8305732		13,152925	
1000,00	9,78		102,259945		14,614362	
1200,00	9,77		122,79481		17,537234	
(x/m)= (akC_e) / ($1+kC_e$)		SLOPE	0,03	1/a	a=	33,3
		INTERCEPT	72,1	1/ak	k=	0,000416
		CORREL	0,9832			
initial phenol (mg/l)	mg phenol/g coal @ 308 K				NEW (Langmuir)	
[C]	x/m		[C] / (x/m)		x/m	
100,00	1,33		75,0525368		1,4614362	
200,00	2,39					
400,00	4,61		86,8475265		5,8457447	
800,00	7,36		108,725197		11,691489	
900,00	8,14		110,602124		13,152925	
1000,00	9,12		109,697236		14,614362	
1200,00	9,05		132,561531		17,537234	
(x/m)= (akC_e) / ($1+kC_e$)		SLOPE	0,04	1/a	a=	25,0
		INTERCEPT	73,0	1/ak	k=	0,00055
		CORREL	0,9653			