Chapter 3

Potential of Anionic Surfactant Modified Alumina in Removal of Phenol from Aqueous Solution

3.1 Introduction

3.1.1 Phenol & Its Properties

Phenols are molecules that have a hydroxyl group attached to the carbon atom of an aromatic ring. By definition, phenol is hydroxybenzene. Phenol is a common name for the compound. Its IUPAC name would be benzenol, derived in the same manner as the IUPAC names for aliphatic alcohols \[1\]. Phenol, also known as carbolic acid and phenic acid, is an organic compound with the chemical formula C\(_6\)H\(_5\)OH. It is a white crystalline solid at room temperature. The molecule consists of a phenyl group (-C\(_6\)H\(_5\)) bonded to a hydroxyl group (-OH). It is mildly acidic, but requires careful handling due to its propensity to cause burns \[2\].

Phenol was first extracted from coal tar, but today is produced on a large scale (about 7 billion kg/year) using a series of industrial processes starting with crude oil. It is an important industrial commodity as a precursor to many materials and useful compounds \[3\]. Its major uses involve its conversion to plastics or related materials. Phenol and its chemical derivatives are key for building polycarbonates, epoxies, Bakelite, nylon, detergents, herbicides such as phenoxy herbicides, and a large collection of pharmaceutical drugs \[2\].

[123]
Figure 3.1: White Crystals of Phenol (A) Structure of Phenol (B).

a. Properties:

Phenol is appreciably soluble in water, with about 8.3 g dissolving in 100 mL (0.88 M). Homogeneous mixtures of phenol and water at phenol to water mass ratios of ~2.6 and higher are also possible. The sodium salt of phenol, sodium phenoxide, is far more water soluble. Phenol does not absorb light at wavelengths >290, phenols react rapidly to sunlit natural water via an indirect reaction with photochemically produced hydroxyl radicals and peroxyl radicals; typical half-lives for hydroxyl and peroxyl radical reactions are on the order of 100 and 19.2 hours of sunlight, respectively. These reactions require dissolved natural organic materials that function as photosensitizers.

b. Acidity

Phenol is slightly acidic. The phenol molecules have weak tendencies to lose the H⁺ ion from the hydroxyl group, resulting in the highly water-soluble phenolate anion C₆H₅O⁻ (also called phenoxide). Compared to aliphatic alcohols, phenol is about 1 million times more acidic, although it is still considered a weak acid. It reacts completely with aqueous NaOH to lose H⁺, whereas most alcohols react only partially. Phenols are less acidic than carboxylic acids, and even carbonic acid.
Table 3.1: Properties of Phenol

<table>
<thead>
<tr>
<th>IUPAC Name</th>
<th>Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Other Names</td>
<td>Carbolic Acid, Benzenol, Phenolic Acid, Hydroxybenzene, Phenic Acid</td>
</tr>
<tr>
<td>Molecular Formula</td>
<td>C₆H₅OH</td>
</tr>
<tr>
<td>Molar Mass</td>
<td>94.11 gm/mol</td>
</tr>
<tr>
<td>Appearance</td>
<td>Transparent Crystalline Solid</td>
</tr>
<tr>
<td>Odor</td>
<td>Sweet &amp; Tarry</td>
</tr>
<tr>
<td>Density</td>
<td>1.07 gm/cm³</td>
</tr>
<tr>
<td>Melting Point</td>
<td>40.5 °C, 314 K, 105 °F</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>181.7 °C, 455 K, 359 °F</td>
</tr>
<tr>
<td>Solubility in Water</td>
<td>8.3 g/100 mL (20 °C)</td>
</tr>
<tr>
<td>Acidity</td>
<td>9.95 (in water), 29.1 (in acetonitrile) [6]</td>
</tr>
<tr>
<td>λ&lt;sub&gt;max&lt;/sub&gt;</td>
<td>270.75 nm [7]</td>
</tr>
</tbody>
</table>

### 3.1.2 Production of Phenol

Because of phenol's commercial importance, many methods have been developed for its production. The dominant current route, accounting for 95% of production (2003), involves the partial oxidation of cumene (isopropylbenzene) via the Hock rearrangement [3].

C₆H₅CH(CH₃)₂ + O₂ → C₆H₅OH + (CH₃)₂CO

Compared to most other processes, the cumene-hydroperoxide process uses relatively mild synthesis conditions, and relatively inexpensive raw materials. However, to operate economically, there must be demand for both phenol, and the acetone by-product.

An early commercial route, developed by Bayer and Monsanto in the early 1900s, begins with the reaction of a strong base with benzenesulfonate [8].

C₆H₅SO₃H + 2 NaOH → C₆H₅OH + Na₂SO₃ + H₂O

Other methods under consideration involve:

- Hydrolysis of chlorobenzene, using base or steam (Raschig-Hooker process) [9].

[125]
C₆H₅Cl + H₂O → C₆H₅OH + HCl

- Direct oxidation of benzene with nitrous oxide, a potentially "green" process:

C₆H₆ + N₂O → C₆H₅OH + N₂

- Oxidation of toluene, as developed by Dow Chemical:

C₆H₅CH₃ + 2 O₂ → C₆H₅OH + CO₂ + H₂O

In the Lummus Process, the oxidation of toluene to benzoic acid is conducted separately.

Phenol is also a recoverable byproduct of coal pyrolysis.[⁹]

3.1.3 Application

The major uses of phenol, consuming two thirds of its production, involve its conversion to precursors to plastics. Condensation with acetone gives bisphenol-A, a key precursor to polycarbonates and epoxide resins. Condensation of phenol, alkylphenols, or diphenols with formaldehyde gives phenolic resins, a famous example of which is Bakelite. Partial hydrogenation of phenol gives cyclohexanone, a precursor to nylon. Nonionic detergents are produced by alkylation of phenol to give the alkylphenols, e.g., nonylphenol, which are then subjected to ethoxylation.[³] Phenol is also a versatile precursor to a large collection of drugs, most notably aspirin but also many herbicides and pharmaceutical drugs. Phenol is also used as an oral anesthetic/analgesic in products such as Chloraseptic or other brand name and generic equivalents, commonly used to temporarily treat pharyngitis. Phenol is so inexpensive that it attracts many small-scale uses. It once was widely used as an antiseptic, especially as carbolic soap, from the early 1900s through the 1970s. It is a component of industrial paint strippers used in the aviation industry for the removal of epoxy, polyurethane and other chemically resistant coatings.[¹⁰] Phenol derivatives are also used in the preparation of cosmetics including sunscreens.[¹¹,¹²]

3.1.4 Pollution Caused by Phenol

Phenols and their derivatives commonly exist in the environment. These compounds are used as the components of dyes, polymers, drugs and other organic substances. The presence of
phenols in the ecosystems is also related with production and degradation of numerous pesticides and the generation of industrial and municipal sewages. Some phenols are also formed during natural processes. These compounds may be substituted with chlorine atoms, may be nitrated, methylated or alkylated. Both phenols and catechols are harmful ecotoxins. Toxic action of these compounds stems from unspecified toxicity related to hydrophobocity and also to the generation of organic radicals and reactive oxygen species. Phenols and catechols reveal peroxidative capacity, they are hematotoxic and hepatotoxic, provoke mutagenesis and carcinogenesis [13]. Presence of phenolic compounds even at low concentration in the industrial waste water adversely affects aquatic as well as human life directly or indirectly when disposed off to public sewage, river or surface water.

3.1.5 Entry of Phenol into the Environment / Source of Phenol

Phenol is released to the air and water as a result of its manufacture, its use in phenolic resins, and organic synthesis [14].

Phenol is found in petroleum products such as coal tar, and creosote and can be released by combustion of wood and auto exhaust. Phenol is also produced by the natural degradation of organic wastes including benzene. Phenol is a major metabolite of benzene, which is found extensively in the environment (Agency for Toxic Substances and Disease Registry 2006), therefore, phenol may be formed in the environment as a result of the natural degradation of benzene [14].

During manufacturing, phenol is released primarily to the atmosphere from storage tank vents and during transport loading (EPA 1979c). Other major sources of release to the atmosphere are residential wood burning and automobile exhaust (EPA 1981a). Volatilization from environmental waters and soils has been shown to be a slow process and is not expected to be a significant source of atmospheric phenol. Phenol is released into the atmosphere from industrial combustion processes. For example, phenol has been detected at a concentration of 0.36 ppb in the emissions of a waste incinerator plant in Germany. Phenol is also found in cigarette smoke and in plastics, but no data are available to determine the extent of exposure to phenol from these sources [15].

Phenol may be released to the soil during its manufacturing process, when spills occur during loading and transport, and when it leaches from hazardous waste sites and landfills.
Generally, data on concentrations of phenol found in soil at sites other than hazardous waste sites are lacking. This may be due in part to a rapid rate of biodegradation and leaching. Phenol can be expected to be found in soils that receive continuous or consistent releases from a point source. Phenol that leaches through soil to groundwater spends at least some time in that soil as it travels to the groundwater. Phenol has been found in groundwater, mainly at or near hazardous waste sites\textsuperscript{15}.

Phenols of anthropogenic origin exist in the environment due to the activity of the chemical, petrol, tinctoral or pharmaceutical industries. The compounds penetrate ecosystems as the result of drainage of the municipal or industrial sewage to surface water\textsuperscript{15}. Moreover, the occurrence of phenols in the environment stems from the production and use of numerous pesticides, in particular phenoxyherbicides like 2,4-dichlorophenoxyacetic acid (2,4-D)\textsuperscript{16}, 4-chloro-2-methylphenoxyacetic acid (MC PA) and also phenolic biocides like pentachlorophenol (PCP)\textsuperscript{17}, dinoseb or diarylether pesticides\textsuperscript{18}. Phenols may occur naturally in aquatic environment from the decomposition of aquatic vegetation. The major anthropogenic sources are industrial effluents and domestic sewage. In 1996, 414 t of phenol were released into the Canadian environment, with 58.5 t being discharged into water, 76% of which was from the pulp, paper, and wood industry. Phenolic wastes may contain cyanide, aldehydes, ketones, alcohols, organic acids, and gases (e.g., as ammonia and carbon dioxide). Phenolic resins, which are used as a binding material in insulation materials, chipboard, paints, and casting sand foundries, are the major source of phenol emissions. These materials contain 2 to >50% phenol, and the emissions are approximately proportional to the concentration of free phenol present as a monomer.

Some phenols may be formed as a result of natural processes like the formation of phenol and p-cresol during decomposition of organic matter or synthesis of chlorinated phenols by fungi and plants\textsuperscript{19}. Phenols are common starting materials and often waste byproducts in the manufacture of industrial and agricultural products. Specially phenolic compounds are often found in wastewaters from coal gasification, coke-oven batteries, refinery and petrochemical plants and other industries, such as synthetic chemicals, herbicides, pesticides, antioxidants, pulp-and-paper, photo developing chemicals, etc.\textsuperscript{20}. The primary sources of phenolic compounds present in industrial effluents are: petroleum refineries, plastic manufacturing plants, pharmaceutical industries, coal carbonization and tar distillation units, wood charcoal production units, coke ovens, phenolformaldehyde plants, bisphenol – A and other synthetic...
resin manufacturing units. Table-3.2 presents some of the industrial waste water comparatively rich with phenol along with their phenol concentration [21]. Phenol also penetrates the environment through vehicle exhaust, and it is used as a disinfectant and reagent in chemical analysis. In the United States alone, are 580,000 people occupationally exposed to phenol influence [22]. Most of the information concerning the aquatic fate of mono- and dihydric phenols refers to the compound phenol [23].

The concentrations of phenol in surface water are different. River water polluted with sewage derived from petrol processing plants contained the concentration of phenol over 40 mg/L [22]. Higher levels of phenol appear to be found in lakes and rivers that serve as water sources and discharge receivers for industrial and population centers, probably as a result of industrial activity and commercial use of phenol-containing products. The presence of phenol in drinking water probably results from using contaminated surface water or groundwater as a source. Its presence in groundwater is probably the result of release to soil, often industrial releases or leachate from waste dumps, and the subsequent leaching of phenol through the soil to the groundwater [24].

Phenols are major by-product of the pulp and paper, mineral (nonmetallic), chemical, steel and metal, and petroleum industries. Phenols are used as disinfectants, biocides, preservatives, dyes, pesticides, and medical and industrial organic chemicals.

Higher levels of phenol appear to be found in lakes and rivers that serve as water sources and discharge receivers for industrial and population centers, probably as a result of industrial activity and commercial use of phenol-containing products. The presence of phenol in drinking water probably results from using contaminated surface water or groundwater as a source. Its presence in groundwater is probably the result of release to soil, often industrial releases or leachate from waste dumps, and the subsequent leaching of phenol through the soil to the groundwater [24].

Phenol has been detected in the effluent discharges of a variety of industries. It was found in petroleum refinery waste water at concentrations of 33.5 ppm and 100 ppb, in the treated and untreated effluent from a coal conversion plant at 4 and 4,780 ppm, respectively, and in shale oil waste water at a maximum of 4.5 ppm. It has also been detected in the effluent from a chemical specialties manufacturing plant at 0.01–0.30 ppm, in effluent from paper mills at
5–8 ppb, and at 0.3 ppm in a 24-hour composite sample from a plant on the Delaware River, 2 and 4 miles downriver from a sewage treatment plant \[24\].

Phenols are also released through automobile exhaust, fireplaces, cigarette smoke, and gases from incinerators. While these do not release directly into water, transfer to water systems may occur, as 1.3–15 μg×L\(^{-1}\) has been found in precipitation \[25\]. Other releases of phenol result from commercial use of phenol and phenol-containing products, including slimicides, general disinfectants, and medicinal preparations such as throat lozenges, mouthwashes, gargles, and antiseptic lotions \[26\].

Phenol is also found in medicinal preparations including throat lozenges, mouthwashes, gargles, and antiseptic lotions. Commercial antiseptic lotions may contain up to 1.4% phenol. Package labeling information indicates that commercial throat lozenges contain up to 29 mg of phenol per lozenge. Other consumer products such as disinfectants and cleaners may contain phenol. It has been found that the smoke of 1 nonfilter cigarette contains 60–140 μg of phenol, 19–35 μg for a filter-tipped cigarette, and 24–107 μg in cigars \[24\].

### Table 3.2: Concentration of Phenolic Compounds in Industrial Waste Water

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Source of Waste Water</th>
<th>Phenol Conc. (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Coal Carbonization Process</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(i) Low Temperature</td>
<td>(i) 1000 – 8000</td>
</tr>
<tr>
<td></td>
<td>(ii) High Temperature</td>
<td>(ii) 800 – 1000</td>
</tr>
<tr>
<td>2.</td>
<td>Metallurgical Coke Manufacturing Process</td>
<td>(i) 900 – 1000</td>
</tr>
<tr>
<td></td>
<td>(i) Spent Liquor after Phenol Recovery</td>
<td>(ii) 35 – 250</td>
</tr>
<tr>
<td></td>
<td>(ii) Coke Oven Effluent</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Oil Refineries</td>
<td>1500 – 2000</td>
</tr>
<tr>
<td>4.</td>
<td>Phenol Formaldehyde Resin Manufacturing Plants</td>
<td>800 – 2000</td>
</tr>
</tbody>
</table>

### Table 3.3: Indian Standards for Drinking Water – Specification (BIS 10500: 1992, Reaffirmed 1993)

<table>
<thead>
<tr>
<th>Substance or Characteristic</th>
<th>Requirement (Desirable Limit)</th>
<th>Permissible Limit (In the Absence of Alternate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>0.001 mg/L</td>
<td>0.002 mg/L</td>
</tr>
</tbody>
</table>
Table 3.4: General Standards for Discharge of Environmental Pollutants (BIS 10500: 1992, Reaffirmed 1993)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Inland Surface Water</th>
<th>Public Sewer</th>
<th>Land of Irrigation</th>
<th>Marine/Coastal Areas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>1.0 mg/L</td>
<td>5.0 mg/L</td>
<td>--</td>
<td>5.0 mg/L</td>
</tr>
</tbody>
</table>

3.1.6 Fate and Behavior of Phenol in the Environment

Sometimes these form complex compounds with metal ions, discharged from other industries, which are more carcinogenic in nature than the Phenolic compounds. The toxicity imparted by phenolic compounds is responsible for health hazards and dangerous to aquatic life [21]. Now the associated problem due to phenol is that when it is present in waste water even in low concentrations can be toxic to some aquatic species and causes taste and odour problems in drinking water. Inhalation and dermal contact of phenol causes cardiovascular diseases and severe skin damage, while ingestion can cause serious gastrointestinal damage and oral administration into laboratory animals has also induced muscle tremors and death. Even short-term application of phenol to the skin can produce blisters and burns in animals. Therefore, the removal of such chemicals from industrial effluents is of great importance [25].

Most of the information concerning the aquatic fate of mono- and dihydric phenols refers to the compound phenol [23]. Phenol is degraded rapidly in air by gas-phase hydroxyl radical reaction (estimated half-life 14.6 hours), but may persist in water for a somewhat longer period. Half-lives for biodegradation range from <1 day in samples of lake water to 9 days in estuarine water. Biodegradation of phenol in water or soil may be hindered or precluded by the presence of high, toxic concentrations of phenol or other chemicals, or by other factors such as a lack of nutrients or microorganisms capable of degrading phenol. If biodegradation is sufficiently slow, phenol in sunlit water will undergo photooxidation with photochemically produced peroxyl radicals, and phenol in soil will leach to groundwater. Phenol may remain in air, water, and soil for much longer periods if it is continually or consistently released to these media from point sources. Since plants can metabolize phenol readily, exposure through eating food derived from plants grown in phenol-containing soil is probably minimal. Phenolic compounds may also come to the environment through the agricultural runoff and domestic waste. Phenolic compounds are water soluble and highly mobile and hence are likely to reach drinking water sources downstream from discharges, where, even at low
concentrations, they can cause severe odour and taste problems and pose risks to populations [25].

Phenol is a major metabolite of benzene, which is found extensively in the environment. Therefore, phenol may be formed in the environment as a result of the natural degradation of benzene. [24]

The biological treatment of waste water containing phenol has shown that <1% of phenol is removed by stripping [24].

Phenol has been reported in sediments at levels as high as 608 ppm dry weight; however, it is not known whether the location of the site where this concentration was reported is at or near a point source of release, such as a hazardous waste dump. The concentrations of the overlying waters were not reported. There is very little sorption of phenol onto aquifer materials [24], suggesting that phenol sorption to sediments may also be minimal. Based on the soil adsorption coefficient, phenol is expected to leach to groundwater; however, the rate of phenol biodegradation in the soil may be so rapid, except in cases of large releases such as spills or continuous releases such as leaching from landfill sites, where the probability of groundwater contamination may be low. Phenol has been detected in groundwater as a result of leaching through soil from a spill of phenol, from landfill sites, and from hazardous waste sites. The sorption coefficient for phenol by soils increases with increasing soil organic matter which may indicate that soil organic matter may be the primary phenol sorbent in soil [24].

Phenol is not expected to bioconcentrate significantly in aquatic organisms. The pKa of phenol is 10, indicating that phenol will primarily exist as the protonated acid at environmental pH values. In alkaline soils and water, phenol will partially exist as an anion, which can affect its fate and transport processes. Although it has been shown that plants readily uptake phenol, bioaccumulation does not take place due to a high rate of respiratory decomposition of phenol to CO₂. [24]

3.1.7 Exposure to Phenol

Populations with potentially high exposure to phenol generally include those who are exposed to relatively highly contaminated environments over long periods of time. These include populations exposed to both identified and unidentified phenol-containing waste disposal
sites and landfills. Populations residing in the vicinity of industries that manufacture or use phenol and large population centers may be exposed to potentially high levels of phenol. Persons who work at establishments that manufacture or use phenol have a risk for high exposure to phenol. Populations that regularly ingest food contaminated with phenol or that regularly ingest or come in contact with phenol-containing products are at risk for high exposure to phenol. Populations that live near a phenol spill site, especially those whose water supply sources are near the spill sites, have a risk for high exposure to phenol. Relatively high exposure may also result from exposure to gaseous emissions from municipal solid waste incinerators and cigarette smoke, although no quantitative data concerning phenol emission from these sources were located. Low income communities and minority populations are more likely to live adjacent to waste disposal sites and landfills where phenol is present [24].

Oral, dermal, and combined oral-dermal exposures are the most likely routes by which children will be exposed to phenol. Oral exposure to low levels of phenol among children is likely because many consumer products contain phenol, particularly in medicines such as gargles, throat lozenges, and others. Products other than medicines that contain phenols include general disinfectants, cleaners, and epoxies [24].

### 3.1.8 Toxicity of Phenol

Phenol and its vapors are corrosive to the eyes, the skin, and the respiratory tract [26]. Repeated or prolonged skin contact with phenol may cause dermatitis, or even second and third-degree burns [27]. Inhalation of phenol vapor may cause lung edema [26]. The substance may cause harmful effects on the central nervous system and heart, resulting in dysrhythmia, seizures, and coma [28]. The kidneys may be affected as well. Long-term or repeated exposure of the substance may have harmful effects on the liver and kidneys [29]. There is no evidence that phenol causes cancer in humans [30]. Besides its hydrophobic effects, another mechanism for the toxicity of phenol may be the formation of phenoxy radicals [31].

Chemical burns from skin exposures can be decontaminated by washing with polyethylene glycol [32], isopropyl alcohol [33], or perhaps even copious amounts of water [34]. Removal of contaminated clothing is required, as well as immediate hospital treatment for large splashes. This is particularly important if the phenol is mixed with chloroform (a commonly-used mixture in molecular biology for DNA & RNA purification).
Phenol toxicity is related with two main processes – unspecified toxicity related with hydrophobocity of the individual compound and formation of free radicals. Hydrophobocity affects the solubility of phenol in a cells’ fractions and thus possibility of interaction of the compound with specified cell and tissue structures. For example, the increase of hydrophobocity of chlorophenols is related to the increasing number of chlorine atoms that enhances toxicity of the individual compound. The strength of toxic influence of the compound also stems from localization of the substitutent. For instance, a chlorine atom substituted in ortho position in phenol molecule decreases its toxicity and meta substitution increases toxic action of the compound. The noxious influence of phenols and their derivatives concerns acute toxicity, histopathological changes, mutagenicity and carcinogenicity.

**a. Acute Toxicity of Phenol**

Phenol irritates skin and causes its necrosis, it damages kidneys, liver, muscle and eyes. Damage to skin is caused by its coagulation related to reaction to phenol with aminoacids contained in keratin of epidermis and collagen in inner skin. In a dose of 1 g phenol may be lethal for an adult man, but individual tolerance for this compound can be high. Some reports reveal that a man can survive even after administration of 30 g of this compound (60 ml of 50% solution). In regard to fast absorption by skin (from 60%-90%) even contact of hand or forehand with phenol solution may cause death. Acute poison with phenol is characterized by dryness in throat and mouth, dark-coloured urine and strong irritation of mucous membranes.

**b. Chronic Toxicity of Phenol**

The investigations showed that chronic administration of phenol by animals leads to pathological changes in skin, esophagus, lungs, liver, kidneys and also urogenital tract. Described changes are mainly induced by lipid peroxidation that is responsible for damage and finally degradation of a cell’s membrane. Chronic exposure of workers to phenol vapours causes anorexia, lost of body weight, weakness, headache, muscles pain and icterus. Phenol is mainly accumulated in brain, kidneys, liver and muscles. Two days after phenol administration it is mainly excreted in unchanged form and also conjugated with sulphates and glucuronides. Catechol is also considered a strong toxin. Doses of 50 to 500 mg/kg of
body weight usually cause death. For mice after oral administration of catechol LD50 is 260 mg/kg of body weight.

### 3.1.9 Treatment of Phenol Containing Water / Waste Water

Various treatment technologies such as adsorption\(^{[40, 41]}\), photodegradation\(^{[42, 43]}\), coagulation flocculation\(^{[44]}\), chemical oxidation\(^{[45]}\), biological process\(^{[46, 47]}\), etc., are available for the removal of phenolic compounds from the wastewater. Biological process is particularly suited to wastewater containing small amount of phenol. Oxidation is used when phenol concentration in wastewater is very high. In coagulation and flocculation process large amount of sludge is generated which may cause disposal problems. Among various physicochemical processes adsorption is widely used for the removal of phenol from wastewater\(^{[40, 48]}\).

### 3.2 Materials & Methodology

#### 3.2.1 Determination of Phenol in Water / Waste Water

**Name of Method:**

4-Aminoantipyrine Method without Chloroform Extraction By Spectrophotometer\(^{[49]}\)

**Principle:**

Phenol, present in the sample, when react with 4-aminoantipyrine at pH =7.9±0.1 in the presence of Potassium Ferrocyanide, form a Red colored antipyrine dye, which is measured at 510 nm wavelength by using spectrophotometer.

**b) Instruments:**

- Semi Micro Digital Weighing Balance (RADWAG-LCGC Make, 308552 Model)
- Visible spectrophotometer (Systronic Make, 1854 Model)

All the reagents used were of AR / LR Grade.
Reagents:

1. **Stock Phenol Solution:**
   
   Dissolve 1.0 gm phenol in freshly boiled and cooled distilled water and dilute to 1 Litre.

   This is 1000 ppm stock solution.

2. **Standard Phenol Solution:**
   
   Dilute 10 ml Stock Phenol solution in distilled water to 1000 ml; 1 ml = 10 ppm Phenol.

   Prepare daily.

3. **Ammonium Hydroxide Solution (0.5 N):**
   
   Dilute 35 ml fresh conc. NH$_4$OH solution to 1 Liter with distilled water.

4. **Phosphate Buffer Solution:**
   
   Dissolve 104.5 gm K$_2$HPO$_4$ and 72.3 gm KH$_2$PO$_4$ in distilled water and dilute to 1 Liter.

   pH should be 6.8.

5. **4-aminoantipyrine Solution:**
   
   Dissolve 2 gm 4-aminoantipyrine in water and dilute to 100 ml. Prepare fresh solution daily for the testing.

6. **Potassium Ferrocyanide Solution:**
   
   Dissolve 8 gm K$_3$Fe(CN)$_6$ in water and dilute to 100 ml.
(A) **Experiment to Determine Phenol by Calibration Curve Method in Water/Wastewater**

- Take 1 ml, 2 ml, 3 ml & 4 ml from standard Phenol solution & make the final volume 100 ml to prepare the standard solutions of 0.1 mg/L, 0.2 mg/L, 0.3 mg/L & 0.4 mg/L standards.

- Add 2.5 ml Ammonium Hydroxide solution.

- Check pH of the solution. Adjust the pH 7.9 ± 1.0 with Phosphate buffer.

- Add 1 ml Potassium Ferrocyanide solution.

- Then add 1 ml 4-Aminoantipyrine solution.

- Make up the volume of each to 100 ml with distilled water. Shake well.

- Keep the solution aside for 15 minutes for the development of Red colour.

- Prepare blank in the same manner with distilled water.

- Set 0 Absorbance & 100% transmittance with blank in spectrophotometer.

- Take absorbance at 510 nm.

- Note down the absorbance & plot the calibration curve.
Table 3.5: Experimental Results of Calibration Curve for Determination of Phenol in Water & Wastewater

<table>
<thead>
<tr>
<th>Standard Conc. (mg/L)</th>
<th>Abs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.000</td>
</tr>
<tr>
<td>0.1</td>
<td>0.014</td>
</tr>
<tr>
<td>0.2</td>
<td>0.026</td>
</tr>
<tr>
<td>0.3</td>
<td>0.043</td>
</tr>
<tr>
<td>0.4</td>
<td>0.055</td>
</tr>
</tbody>
</table>

*Calculation of sample by using calibration curve:

\[
\text{mg/L Phenol} = \left( \frac{A}{B} \right) \times 1000
\]

Where,

A = mg of Phenol from calibration curve
B = ml of original sample

Figure 3.2: Calibration Curve for Phenol Determination in Water & Wastewater

\[
y = 0.1383x \\
R^2 = 0.9973
\]
(B) **Experimental Procedure**

- Take suitable quantity of sample. Select the sample quantity such that it does not contain more than 0.5 mg of Phenol.
- Add 2.5 ml Ammonium Hydroxide solution.
- Check pH of the solution. Adjust the pH $7.9 \pm 1.0$ with Phosphate buffer.
- Add 1 ml Potassium Ferrocyanide solution.
- Then add 1 ml 4-Aminoantipyrine solution.
- Make up the volume of each to 100 ml with distilled water. Shake well.
- Keep the solution aside for 15 minutes for the development of Red colour.
- Take absorbance at 510 nm.

### 3.2.2 Preparation of Anionic Surfactant Modified Alumina (ASMA)

- 20,000 mg/L SDS in 500 ml standard measuring flask was prepared.
- Volume of the solution was 500 ml.
- 100 gm/L Alumina was added in the flask.
- Adjusted pH 4 with 1N HCl & 1N NaOH.
- The flask was kept on magnetic stirrer for 24 Hrs to determine reproducibility.
- After completion of shaking period, filtered out contents of the flasks through ordinary filter paper.
- Then the filtered solid material (100 gm/L + surfactant), remaining on the filter paper, was gently washed first with tap water & then with distilled water.
- The washed solid material was then dried in hot air oven at 60 °C for 24 Hrs.
- This oven dried solid powder is Anionic Surfactant Modified Alumina (ASMA).
- ASMA powder was stored in plastic bottle for its further use in the removal of organic pollutant like Phenol, Crystal Violet Dye etc. from waste water by adsolubilization method.
3.2.3 Factors Affecting Removal of Phenol by ASMA from Aqueous Solution

3.2.3(A) Experimental Set Up to Study Effects of pH

- 500 mg/L Phenol stock solution was prepared.
- 100 ml quantity solution of high initial concentration i.e. 500 mg/L Phenol was taken in 250 ml beaker.
- Such 5 numbers of sets were prepared.
- Adsorbent i.e. ASMA Dosage was adjusted 12 gm/L & added it to previously prepared Phenol solution. As here quantity is 100 ml, add 1.2 gm of ASMA to the previously prepared 500 mg/L Phenol solution.
- pH of the beakers were adjusted 2, 4, 6, 8, 10 respectively by adding the required amount of 1N HCl and 1N NaOH.
- Beakers were kept on the magnetic stirrer for 1.5 Hrs.
- After completion of reaction time, contents in the beakers were allowed to settle down for 5 minutes.
- Supernatant was filtered through ordinary filter paper & filtrate was collected to check the final concentration of Phenol by using above mentioned 4-Amino Antipyrine Method without Chloroform Extraction Method.
- Readings were recorded & Graph was plotted to get equilibrium pH value.

Figure 3.3: Experimental Set up to Study Effects of pH on Removal of Phenol by ASMA
3.2.3(B) Experimental Set up to Study Effects of Contact Time

- 100 ml solution of high initial concentration i.e. 500 mg/L Phenol was taken in 250 ml beaker.
- Such 4 numbers of sets were prepared.
- Dosage of the adsorbent was adjusted 12 gm/L & added it to previously prepared Phenol solution.
- PH 4 (i.e. equilibrium pH resulted from experiment 3.2.3(A)) was adjusted of all the beakers by adding the required amount of 1N HCl & 1N NaOH.
- Beakers were kept on the magnetic stirrer for 30 minutes, 60 minutes, 90 minutes & 120 minutes.
- Beakers were allowed to stay for 5 minutes after completion of reaction time.
- Supernatant was filtered through ordinary filter paper & filtrate was collected to check the final concentration of Phenol by using above mentioned 4-Amino Antipyrine Method Without Chloroform Extraction Method.
- Readings were recorded & Graph was plotted to get equilibrium contact time.

![Diagram](image)

Figure 3.4: Experimental Set Up to Study Effects of Contact Time on Removal of Phenol by ASMA
3.2.3(C) Experimental Set up to Study Effects of Adsorbent i.e. ASMA Dosage

- 100 ml solution of high initial concentration i.e. 61 mg/L Phenol was taken in 250 ml beaker.
- Dosage of the adsorbent varied 12gm/L, 25gm/L & 40gm/L.
- PH 4 (i.e. equilibrium pH resulted from experiment 3.2.3(A)) was adjusted of all the beakers by adding the required amount of 1N HCl & 1N NaOH.
- Beakers were kept on the magnetic stirrer for 1.5hrs (i.e. equilibrium Contact Time resulted from the experiment 3.2.3(B)).
- Beakers were allowed to stay for 5 minutes after shaking time.
- Supernatant was filtered through ordinary filter paper & filtrate was collected to check the final concentration of Phenol by using above mentioned 4-Amino Antipyrine Method without Chloroform Extraction Method.
- Readings were recorded & Graph was plotted.

![Figure 3.5: Experimental Set Up to Study Effects of Adsorbent Dosage on Removal of Phenol by ASMA](image-url)
3.2.3(D) Experimental Set up to Study Effects of Adsorbate i.e. Phenol Concentration

- 100 ml solution of variable Phenol conc. Viz. 50 mg/L & 70 mg/L from 100 mg/L stock solution of Phenol in 250 ml beakers were taken.
- Dosage of the adsorbent was kept 12 gm/L (i.e. equilibrium resulted from experiment 3.2.3(C)) & added it to previously prepared Phenol solution.
- PH 4 (i.e. equilibrium pH resulted from experiment 3.2.3(A)) was adjusted of all the beakers by adding the required amount of 1N HCl & 1N NaOH.
- Beakers were kept on the magnetic stirrer for 1.5hrs (i.e. equilibrium Contact Time resulted from experiment 3.2.3(B)).
- Beakers were allowed to stay for 5 minutes after completion of reaction time.
- Supernatant was filtered through ordinary filter paper & filtrate was collected to check the final concentration of Phenol by using above mentioned 4-Amino Antipyrine Method without Chloroform Extraction Method.
- Readings were recorded & graph was plotted.

![Figure 3.6: Experimental Setup to Study Effects of Initial Adsorbate Conc. on Removal of Phenol by ASMA](image-url)
3.2.3(E) Effect of Temperature

- 100 ml solution of high initial concentration i.e. 50 mg/L was taken in 250 ml beaker.
- Such 3 numbers of sets were prepared to study the effect of temperature (30°C, 40°C & 50°C) in removal of Phenol by ASMA.
- Dosage of the adsorbent was adjusted 40 gm/L & added it to previously prepared Phenol solution.
- PH 4 (i.e. equilibrium pH resulted from the experiment 3.2.3(A)) kept constant of all the beakers by adding the required amount of 1N HCl & 1N NaOH.
- 30°C, 40°C & 50°C temperature set on the magnetic stirrers.
- Beakers were kept on the magnetic stirrer for 1.5 Hrs.
- Beakers were allowed to stay for 5 minutes after shaking time.
- Supernatant was filtered through ordinary filter paper & filtrate was collected to check the final concentration of Phenol by using above mentioned 4-Amino Antipyrine Method without Chloroform Extraction Method.
- Readings were recorded & Graph was plotted to get equilibrium temperature.

Figure 3.7: Experimental Setup to Study Effects of Temperature on Removal of Phenol by ASMA

12 gm/L ASMA
61 mg/L Phenol + 1.5 Hrs Contact Time
pH 4

25 gm/L ASMA
61 mg/L ASMA + 1.5 Hrs Contact Time
pH 4

40 gm/L ASMA
61 mg/L Phenol + 1.5 Hrs Contact Time
pH 4

[144]
3.2.4 Chemical Kinetic Study

- 100 ml solution of high initial concentration i.e. 500 mg/L Phenol was taken in 250 ml beaker.
- Such 4 numbers of sets were prepared.
- Dosage of the adsorbent was adjusted 12 gm/L & added it to previously prepared Phenol solution.
- PH 4 (i.e. equilibrium pH resulted from experiment 3.2.3(A)) was adjusted of all the beakers by adding the required amount of 1N HCl & 1N NaOH.
- Beakers were kept on the magnetic stirrer for 30 minutes, 60 minutes, 90 minutes & 120 minutes.
- Beakers were allowed to stay for 5 minutes after completion of reaction time.
- Supernatant was filtered through ordinary filter paper & filtrate was collected to check the final concentration of Phenol by using above mentioned 4-Amino Antipyrine Method Without Chloroform Extraction Method.
- Readings were recorded & Graph was plotted.

Following Kinetic Models were studied in detail.

1) **Pseudo First Order Model**

The pseudo-first order kinetic model based on the adsorbent for sorption analysis is of the form:

$$\log (q_e - q_t) = \log q_e - (k_1/2.303) t$$

Where,

$q_e$ (mg/gm)is the mass of Monocrotophos adsorbed at equilibrium

$q_t$ (mg/gm) the mass of Monocrotophos at any time (t) & $K_1$ (min$^{-1}$) is the equilibrium rate constant of pseudo-first order adsorption.

The values of $k_1$ & $q_e$ are determined from the slope & intercept of the plot of $\log (q_e - q_t)$ versus $t$, respectively.$^{[80]}$
2) Pseudo Second Order Model

A pseudo-second order rate expression based on the sorption equilibrium capacity may be represented as:

\[
t / q_t = 1/ k_2 q_e^2 + (1/ q_e) t
\]

Where,

\( k_2 \) is the pseudo-second order rate constant (g mg\(^{-1}\) min\(^{-1}\)) \[^{[50]}\].

The value of \( q_e \) is determined from the slope of the plot of \( t / q_t \) versus \( t \).

3) Intraparticle Diffusion

In order to understand the mechanism involved in the sorption process the kinetics experimental results were fitted to the Weber’s intraparticle diffusion (Weber and Morris, 1963) model. It is reported that if intraparticle diffusion is involved in the process then a plot of adsorbate uptake vs. the square root of time would result in a linear relationship and the intraparticle diffusion would be the rate limiting step if this line passes through the origin. Thus the kinetics results were analyzed by the Intraparticle diffusion model which is expressed as

\[
q_t = k_{id} t^{1/2} + C
\]

Where,

\( C \) is the intercept

\( K_{id} \) is the intra-particle diffusion rate constant.

The intra-particle diffusion rate constant was determined from the slope of linear gradients of the plot \( q_t \) versus \( t^{1/2} \) \[^{[50]}\].
3.2.5 Batch Isotherm Studies

Isotherm experiments were conducted to investigate the relationship between the solid phase concentration of an adsorbate & the solution phase concentration of the adsorbate at an equilibrium condition. The removal percentage (R %) of Phenol was calculated for each run by following equation:

\[ R (\%) = \left[ \frac{(C_i - C_e)}{C_i} \right] \times 100 \]

Where, Ci and Ce are the initial & final concentration of Phenol (mg/L) in the solution. The adsorption capacity of the adsorbent for each concentration of Phenol at equilibrium was calculated using following equation:

\[ q_e (\text{mg/g}) = \left[ \frac{(C_i - C_e)}{M} \right] \times V \]

Where, Ci & Ce were the initial & final concentration of Phenol (mg/L) in the test solution respectively. V is the volume of solution (in Liter) & M is the mass of adsorbent (gm).

3.2.6 Adsorption Isotherm Studies

In the present study, various adsorption isotherm models have been used to study the adsorption capacity and equilibrium coefficients for adsorption. Four commonly used isotherms (viz. Langmuir, BET, Freundlich and Temkin isotherm) were studied.

1. The Langmuir Adsorption Isotherm

In the years 1916-1918 Langmuir developed the adsorption theory in its modern form. Langmuir isotherm equation is derived from simple mass kinetics, assuming chemisorption. The derivation of the Langmuir adsorption isotherm involves four implicit assumption: a) the adsorption is at a fixed number of definite, localized sites; b) monolayer adsorption is formed on the surface of adsorbent; c) the surface is homogenous, that is, the affinity of each binding site for gas molecules is the same; d) there is no lateral interaction between adsorbate molecules. Alternatively at higher concentrations, it predicts a monolayer sorption capacity. It assumes that the uptake of adsorbate occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The commonly expressed form is:
\[ \frac{C_e}{q_e} = \left[ \frac{1}{Q_0 b} + \frac{1}{Q_0} \times C_e \right] \]

Where, \( C_e \) is the equilibrium concentration of adsorbate (mg/L) and \( q_e \) is the amount of adsorbate adsorbed per gram at equilibrium (mg/g). \( Q_0 \) (mg/g) and \( b \) (L/mg) are Langmuir constants related to adsorption capacity and rate adsorption, respectively. The values of \( Q_0 \) and \( b \) were calculated from the slope and intercept of the Langmuir plot of \( C_e \) versus \( C_e/q_e \) \[^{[51]}\].

The Langmuir adsorption isotherm has the simplest form and shows reasonable agreements with a large number of experimental isotherms. Therefore, the Langmuir adsorption model is probably the most useful one among all isotherms describing adsorption, and often serves as a basis for more detailed developments \[^{[52]}\].

2. Freundlich Isotherm

Boedecker proposed in 1895 an empirical adsorption equation known as Freundlich isotherm, because Freundlich assigned great importance to it and popularized its use. It is frequently found that data on adsorption from a liquid phase are fitted better by the Freundlich isotherm equation, provided that the adsorption sites are not identical, and the total adsorbed amount is the same over all types of sites. The Freundlich isotherm is expressed as:

\[ \log_{10} q_e = \log_{10}(K_f) + \left( \frac{1}{n} \right) \log_{10} (C_e) \]

Where, \( q_e \) is the amount of adsorbate adsorbed at equilibrium (mg/g), and \( C_e \) is the equilibrium concentration of adsorbate in solution (mg/L). \( K_f \) and \( n \) are the constants incorporating all factors affecting the adsorption process \[^{[51]}\].

The Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. According to Freundlich equation, the amount adsorbed increases infinitely with increasing concentration or pressure. This equation is, therefore, unsatisfactory for high coverage. At low concentration, this equation does not reduce to the linear isotherm. In general, a large number of the experimental results in the field of van der Walls adsorption can be expressed by means of the Freundlich equation in the middle concentration range \[^{[51]}\].
3. **Temkin Isotherm**

Temkin isotherm model is given by the following equation:

\[ X = a + b \ln C \]

Where, \( C \) is the equilibrium concentration of solution (mg/L), \( X \) is amount of adsorbate adsorbed per gram weight of adsorbent (mg/g), \( a \) and \( b \) are constants related to adsorption capacity and intensity of adsorption and related to the intercept and slope of the plots of \( \ln C \) versus \( X \) [53].

4. **BET Isotherm**

BET isotherm was developed by Brunauer, Emmett and Teller as an extension of Langmuir isotherm, which assumes that first layer of molecules adhere to the surface with energy comparable to heat of adsorption for monolayer sorption and subsequent layers have equal energies. Equation in its linearized form expressed as:

\[
\frac{C_f}{(C_f-C_s)} q = \frac{1}{B q_{\text{max}}} - \left( \frac{B - 1}{B q_{\text{max}}} \right) \left( \frac{C_f}{C_s} \right)
\]

Where, \( C_s \) is the saturation concentration (mg/L) of the solute, \( C_f \) is solute equilibrium concentration. \( B \) and \( q_{\text{max}} \) are two constants and can be evaluated from the slope and intercept [54].
3.3 Results & Discussion

3.3.1(A) Effect of pH

Studies were carried out to see the effect of pH in the range of 2–10. The pH of the solutions was maintained by adding HCl or NaOH. The removal of phenol decreases with the increase of pH. At lower pH phenol is adsolubilized as molecular form. As pH increases phenol is converted into negatively charged phenolate ion and the negatively charged head groups of SDS molecules adsorbed on the alumina surface repel these ions. At pH > 9.15 SDS molecules are desorbed from the alumina surface and cause reduction in the phenol removal [55]. Here in below figure 3.9 it is shown that maximum removal of Phenol was obtained from experimental data i.e. 18.7 % and adsorption capacity (q, i.e. 8mg/gm) at pH 4.

Table 3.6: Effect of pH on Adsorption of Phenol by ASMA from Aqueous Solution

<table>
<thead>
<tr>
<th>High initial conc. of Phenol (mg/L)</th>
<th>Adsorbent Dosage Gm/L</th>
<th>Contact Time (Hr)</th>
<th>pH Range</th>
<th>Absorbance (mg of Phenol from graph (Sample Abs/0.1383))</th>
<th>Final Conc. of Phenol (mg/L) from Calibration Curve*</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>12</td>
<td>1.5</td>
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<td>0.035 0.3</td>
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<td></td>
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<td>6</td>
<td>0.037 0.3</td>
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<td>8</td>
<td>0.036 0.3</td>
<td>52.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>0.040 0.3</td>
<td>57.6</td>
</tr>
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</table>

Figure 3.8: Effect of pH on Adsorption of Phenol by ASMA from Aqueous Solution
Table 3.7: % Removal of Phenol & Adsorption Capacity of ASMA at Different pH:

<table>
<thead>
<tr>
<th>High initial conc. of Phenol (mg/L)</th>
<th>Adsorbent Dosage Gm/L</th>
<th>Contact Time (Hr)</th>
<th>pH Range</th>
<th>% Removal</th>
<th>Adsorption Capacity qₑ (mg/gm)</th>
</tr>
</thead>
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<tr>
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<td><strong>0.95</strong></td>
</tr>
<tr>
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<td>6</td>
<td>12.6</td>
<td>0.64</td>
</tr>
<tr>
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<td>8</td>
<td>14.3</td>
<td>0.73</td>
</tr>
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<td></td>
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<td></td>
<td>10</td>
<td>5.6</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Figure 3.9: Effect of pH on % Removal of Phenol by ASMA
3.3.1(B) Effect of Contact Time

Agitation time or contact time is one of the effective factors in batch adsorption was studied in time span of 0.5 to 2.0 Hrs. Contact time 1.5Hr was found equilibrium for adsorption of Phenol on ASMA. Almost 18.5% removal was observed at 12 gm ASMA dosage and 4 pH. After 1.5 Hr. it was decreasing. This decrease in the adsorption rate may be due to a distribution of surface sites that cause decrease in adsorbent- adsorbate interaction with increasing surface density \[51\]. It may be explained by the fact that adsorbate molecules attain the equilibrium at a particular pH, dose and time, adsorption got slowed down in later stages, because initially a number of vacant surface sites may be available for adsorption and after some time, the remaining vacant surface site may be exhausted due to repulsive forces between the molecules of adsorbate and counter ion binding at the surface of the adsorbent \[50\].

Table 3.8: Effect of Contact Time on Adsorption of Phenol by ASMA from Aqueous Solution

<table>
<thead>
<tr>
<th>High initial conc. of Phenol (mg/L)</th>
<th>Adsorbent Dosage Gm/L</th>
<th>Equilibrium pH</th>
<th>Contact Time (Min.)</th>
<th>Absorbance</th>
<th>mg of Phenol from calibration curve (Sample Abs/0.1383)</th>
<th>Final Conc. of Phenol (mg/L) from Calibration Curve *</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>12</td>
<td>4</td>
<td>30</td>
<td>0.039</td>
<td>0.3</td>
<td>56.6</td>
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<td>60</td>
<td>0.036</td>
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<td></td>
<td>90</td>
<td>0.034</td>
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<td>49.6</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>120</td>
<td>0.038</td>
<td>0.3</td>
<td>55.0</td>
</tr>
</tbody>
</table>

Figure 3.10: Effect of Contact Time on Adsorption of Phenol by ASMA from Aqueous Solution
Table 3.9: % Removal of Phenol & Adsorption Capacity of ASMA at Different Contact Time

<table>
<thead>
<tr>
<th>High initial conc. of Phenol (mg/L)</th>
<th>Adsorbent Dosage Gm/L</th>
<th>Equilibrium pH</th>
<th>Contact Time (Min.)</th>
<th>% Removal</th>
<th>Adsorption Capacity $q_e$ (mg/gm)</th>
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</thead>
<tbody>
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<td>7.0</td>
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<td>13.9</td>
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<td></td>
<td>90</td>
<td>18.5</td>
<td><strong>0.94</strong></td>
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<tr>
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<td>120</td>
<td>9.8</td>
<td>0.50</td>
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</tbody>
</table>

Figure 3.11: Effect of Contact Time on % Removal of Phenol by ASMA
3.3.1(C) Effect of Adsorbent Dosages

The effect of adsorbent dose on the adsorption of Phenol by ASMA is presented in below figure 3.12(A). From the experiments it was observed that adsorption increases with the increase of ASMA dosage. % Removal of Phenol increases from 32 % to 85 % as the ASMA dosage increases from 12 gm/L to 36 gm/L (36 gm/L i.e. addition of fresh 12gm/L adsorbent dosage for three times). Here, the experiment study was performed in two ways. One is shown above. In the other way 12 gm/L adsorbent – ASMA dosage was provided for the removal of 61 mg/L Phenol. pH was adjusted 4 & 1.5 Hr Contact Time was given. After completion of reaction time, 2 ml supernatant was taken & Phenol conc. was measured. Then again in the same beaker 12 gm/L ASMA dosage was done & same process followed for 1.5 Hr. Again Phenol conc. was measured for 2 ml supernatant. Same cycle was repeated for third time also & Phenol conc. was measured. It was observed that in the other (2nd) way the adsorption rate was observed very high then in the 1st way because here in the 2nd way all the time fresh ASMA was provided. It ultimately increases the surface area & enhances the removal of Phenol. In the first way it was observed that the Phenol adsorption increases with the increase in adsorbent dosage. Phenol % removal was observed from 32% to 66% for the 1st way. Where as in the 2nd way from 32% to 85% removal of Phenol was observed. The surface area is directly proportional to the dose of the adsorbent in the system [56]. Higher the dose of adsorbent in the solution, greater is the availability of exchangeable sites for metal ions and greater is the surface area [57]. Therefore with increasing Alumina dosage per gm adsorption capacity is decreasing. From the results, the equilibrium adsorbent ASMA dosage is 40 gm/L. At the dosage of 40 gm/L, the maximum 66% & 85% Phenol removal were observed in 1st & 2nd ways respectively.
Table 3.10(A): Effect of Adsorbent Dosage on Adsorption of Phenol by ASMA from Aqueous Solution

<table>
<thead>
<tr>
<th>High initial conc. of Phenol (mg/L)</th>
<th>Equilibrium Contact Time (Hr)</th>
<th>Equilibrium pH</th>
<th>Adsorbent Dosage Gm/L</th>
<th>Absorbance</th>
<th>mg of Phenol from calibration curve (Sample Abs/0.1383)</th>
<th>Final Conc. of Phenol (mg/L) from Calibration Curve *</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>1.5</td>
<td>4</td>
<td>12</td>
<td>0.028</td>
<td>0.2</td>
<td>41</td>
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<td></td>
<td></td>
<td>25</td>
<td>0.019</td>
<td>0.1</td>
<td>28</td>
</tr>
</tbody>
</table>

Figure 3.12(A): Effect of Adsorbent Dosage Variable in Removal of Phenol by ASMA

Figure 3.12(A): Effect of Adsorbent Dosage on Removal of Phenol by ASMA from Aqueous Solution
Table 3.11(B): Cumulative Effect of Adsorbent Dosage & Contact Time on Adsorption of Phenol by ASMA from Aqueous Solution

<table>
<thead>
<tr>
<th>High initial conc. of Phenol (mg/L)</th>
<th>Equilibrium Contact Time (Hr)</th>
<th>Equilibrium pH</th>
<th>Adsorbent Dosage Gm/L</th>
<th>Absorbance</th>
<th>mg Phenol from calibration curve (Sample Abs/0.1383)</th>
<th>Final Conc. of Phenol (mg/L) from Calibration Curve *</th>
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</thead>
<tbody>
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<td>61</td>
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<td>12</td>
<td>0.028</td>
<td>0.2</td>
<td>41</td>
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</tr>
<tr>
<td>Above 1.5 + 1.5</td>
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<td></td>
</tr>
<tr>
<td>Above 1.5 + 1.5</td>
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<td>Above exposed 12gm/L</td>
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<td>0.1</td>
<td>28</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>ASMA + 12 gm/L fresh ASMA</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Above 3 + 1.5</td>
<td></td>
<td>Above exposed 24</td>
<td>0.006</td>
<td>0.04</td>
<td>9</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>gm/L ASMA + 12</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>gm fresh ASMA</td>
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Figure 3.13(B): Cumulative Effect of Adsorbent Dosage & Contact Time on Removal of Phenol by ASMA from Aqueous Solution
Table 3.12(A): % Removal of Phenol & Adsorption Capacity of ASMA at Different Adsorbent Dosage

<table>
<thead>
<tr>
<th>High initial conc. of Phenol (mg/L)</th>
<th>Equilibrium Contact Time (Hr)</th>
<th>Equilibrium pH</th>
<th>Adsorbent Dosage (Gm/L)</th>
<th>% Removal</th>
<th>Adsorption Capacity q_e (mg/gm)</th>
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</thead>
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<td>12</td>
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<td>1.6</td>
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<td>25</td>
<td>54</td>
<td>2.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>66</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Figure 3.14(A): Effect of Adsorbent Dosages on % Removal of Phenol by ASMA
Table 3.13(B): % Removal of Phenol & Adsorption Capacity of ASMA at Different Adsorbent Dosage

<table>
<thead>
<tr>
<th>High initial conc. of Phenol (mg/L)</th>
<th>Equilibrium Contact Time (Hr)</th>
<th>Equilibrium pH</th>
<th>Adsorbent Dosage Gm/L</th>
<th>% Removal</th>
<th>Adsorption Capacity q_e (mg/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>1.5</td>
<td>4</td>
<td>12</td>
<td>32</td>
<td>1.6</td>
</tr>
<tr>
<td>Above 1.5 + 1.5</td>
<td></td>
<td></td>
<td>Above exposed 12gm/L ASMA + 12 gm/L fresh ASMA</td>
<td>54</td>
<td>1.6</td>
</tr>
<tr>
<td>Above 3 + 1.5</td>
<td></td>
<td></td>
<td>Above exposed 24 gm/L ASMA + 12 gm fresh ASMA</td>
<td>85</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Figure 3.15(B): Effect of Adsorbent Dosages on % Removal of Phenol by ASMA
3.3.1(D) Effect of Initial Adsorbate (Phenol) Concentration

The effect of initial concentration of adsorbate Phenol on the adsorption was studied. Here, adsorbent dose was kept 40 gm/L, pH 4 was adjusted, contact time was given 1.5 Hrs. Initial concentration of Phenol was varied 50 ppm & 70 ppm. Final conc. of Phenol is 15 mg/L & 20 mg/L, when the high initial conc. is 50 mg/L & 70 mg/L respectively. % Removal efficiency was almost same i.e. 70 % for both the concentrations. The results show that no major change occurs at different initial concentration. It is almost same for all conc. of Phenol. Adsorption capacity i.e. $q_e$ is 0.88 mg/gm & 1.25 mg/gm for 50 mg/L & 70 mg/L initial Phenol conc. respectively.

Table 3.14: Effect of Initial Adsorbate Concentration on Adsorption of Phenol by ASMA from Aqueous Solution

<table>
<thead>
<tr>
<th>Equilibrium Adsorbent Dosage (Gm/L)</th>
<th>Equilibrium Contact Time (Hr)</th>
<th>Equilibrium pH</th>
<th>High initial conc. of Phenol (mg/L)</th>
<th>Absorbance</th>
<th>mg of Phenol from calibration curve (Sample Abs/0.1383)</th>
<th>Final Conc. of Phenol from Calibration Curve (mg/L) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1.5</td>
<td>4</td>
<td>50</td>
<td>0.010</td>
<td>0.07</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>70</td>
<td>0.014</td>
<td>0.1</td>
<td>20</td>
</tr>
</tbody>
</table>

Figure 3.16: Effect of Adsorbate Conc. on Adsorption of Phenol by ASMA from Aqueous Solution
Table 3.15: % Removal of Phenol & Adsorption Capacity of ASMA at Different Initial Adsorbate Conc.

<table>
<thead>
<tr>
<th>Equilibrium Adsorbent Dosage (Gm/L)</th>
<th>Equilibrium Contact Time (Hr)</th>
<th>Equilibrium pH</th>
<th>High initial conc. of Phenol (mg/L)</th>
<th>Final Conc. of Phenol (mg/L) from Calibration Curve</th>
<th>% Removal</th>
<th>Adsorption Capacity q_e (mg/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1.5</td>
<td>4</td>
<td>50</td>
<td>15</td>
<td>70</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>70</td>
<td>20</td>
<td>71</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Figure 3.17: Effect of Initial Adsorbate Conc. on % Removal of Phenol by ASMA

3.3.1(E) Effect of Temperature

Thermodynamics study was also carried out to study the effect of temperature on the % removal of Phenol. For the study purpose, 3 sets were prepared. Temperature range viz. 30 °C, 40 °C & 50 °C were adjusted by knob of magnetic stirrer. Here adsorbent dosage 40 gm/L & pH 4 respectively for all the sets. Results show that temperature had no effect on the Phenol removal.
Table 3.16: Effect of Temperature on Adsorption of Phenol by ASMA from Aqueous Solution

<table>
<thead>
<tr>
<th>High initial conc. of Phenol (mg/L)</th>
<th>Equilibrium Contact Time (Hr)</th>
<th>Equilibrium pH</th>
<th>Adsorbent Dosage Gm/L</th>
<th>Temp (°C)</th>
<th>Absorbance</th>
<th>mg of Phenol from calibration curve (Sample Abs/0.1383)</th>
<th>Final Conc. of Phenol (mg/L) from Graph *</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.5</td>
<td>4</td>
<td>40</td>
<td>30</td>
<td>0.010</td>
<td>0.07</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>0.011</td>
<td>0.08</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>0.010</td>
<td>0.07</td>
<td>15.0</td>
</tr>
</tbody>
</table>

Figure 3.18: Effect of Temperature on Removal of Phenol by ASMA
Table 3.17: % Removal of Phenol & Adsorption Capacity of ASMA at Different Temperature.

<table>
<thead>
<tr>
<th>High initial conc. of Phenol (mg/L)</th>
<th>Equilibrium Contact Time (Hr)</th>
<th>Equi. pH</th>
<th>Adsorbent Dosage Gm/L</th>
<th>Temp. (°C)</th>
<th>Final Conc. of Phenol (mg/L) from Graph</th>
<th>% Removal</th>
<th>Adsorption Capacity qₑ (mg/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.5</td>
<td>4</td>
<td>40</td>
<td>30</td>
<td>15.0</td>
<td>70</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>15.2</td>
<td>70</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>15.0</td>
<td>70</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Figure 3.19: Effect of Temperature on % Removal of Phenol by ASMA
3.3.2 Chemical Kinetic Study

Chemical kinetics is also known as reaction kinetics. It is the study of rates of chemical processes. It includes investigations of how different experimental conditions can influence the speed of a chemical reaction. In order to investigate the controlling mechanism of adsorption process such as mass transfer & chemical reaction, a suitable kinetic model is needed to analyze the data. In the present study, three kinetic models have been tested in order to predict the adsorption data of ASMA as a function of time using a Pseudo-first order, pseudo-second order kinetic models & intra-particle diffusion model.

Table 3.18: Results of Kinetic Study

<table>
<thead>
<tr>
<th>High initial conc. of Phenol (mg/L)</th>
<th>Equilibrium pH</th>
<th>Adsorbent Dosage (Gm/L)</th>
<th>Time Interval (min.)</th>
<th>Final Conc. of Phenol (mg/L) from Graph</th>
<th>Adsorption Capacity (qe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>4</td>
<td>12</td>
<td>30</td>
<td>56.6</td>
<td>0.36</td>
</tr>
<tr>
<td>60</td>
<td>52.4</td>
<td>0.71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>49.6</td>
<td>0.94</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>55.0</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) Pseudo-First Order Model

Log (q_e - q_t) = log q_e – (k_1/2.303) t

Where, q_e (mg/gm) is the mass of Phenol adsorbed at equilibrium, q_t (mg/gm) the mass of Phenol adsorbed at any time (t) & k_1 (min^{-1}) is the equilibrium rate constant of pseudo-first order adsorption. The values of k_1 & q_e are determined from the slope & intercept of the plot of Log (q_e - q_t) versus t, respectively \(^{[50]}\).
Table 3.19: Data Required for Pseudo First Order Kinetic Model Calculation

<table>
<thead>
<tr>
<th>Time Interval (min.)</th>
<th>Final Conc. of Phenol (mg/L) from Graph</th>
<th>Adsorption Capacity qt (mg/gm)</th>
<th>(qe-qt)</th>
<th>Log (qe – qt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>56.6</td>
<td>0.36</td>
<td>0.94 – 0.36 = 0.58</td>
<td>0.2366</td>
</tr>
<tr>
<td>60</td>
<td>52.4</td>
<td>0.71</td>
<td>0.94 – 0.71 = 0.23</td>
<td>0.6383</td>
</tr>
<tr>
<td>90</td>
<td>49.6</td>
<td>0.94 = qe</td>
<td>0.94 – 0.94 = 0.00</td>
<td>0.000</td>
</tr>
<tr>
<td>120</td>
<td>55.0</td>
<td>0.50</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Where, qe (mg/gm) = Mass of Phenol Adsorbed, qt (mg/gm) = Mass of Phenol at particular time

\[ qe = \frac{\text{Initial Conc. of Phenol} - \text{Final Conc. of Phenol}}{M} \times V \]

Where, V is the volume of solution (in Liter) & M is the mass of adsorbent (gm) \[^{[51]}\].

Table 3.20: Pseudo First Order Kinetic Study

<table>
<thead>
<tr>
<th>Time Interval (min.)</th>
<th>Log (qe – qt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>-0.2366</td>
</tr>
<tr>
<td>60</td>
<td>-0.6383</td>
</tr>
<tr>
<td>90</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Figure 3.20: Pseudo First Order Kinetic Study for Phenol Adsorption on ASMA
• Calculation from Graph

K1/2.303 = Slope

Where, Slope from Graph = 0.0039

i.e. K1 = 0.0039 * 2.303 = 0.0090

qe (calculated) = Antilog (intercept from graph) = Antilog (-0.5282) = 0.2964 i.e. 0.30

Table 3.21: Pseudo First Order Kinetic Parameters for Phenol Adsorption on ASMA

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>qe (mg/gm) (Exp.)</th>
<th>qe (mg/gm) (Cal.)</th>
<th>K1 (min⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASMA</td>
<td>0.94</td>
<td>0.30</td>
<td>0.0090</td>
<td>0.13</td>
</tr>
</tbody>
</table>

From the above study it was observed that the present adsolubilization process does not follows pseudo first order kinetic model. The experimental qe is 0.94 mg/gm & calculated qe value was obtained 0.30 mg/gm. As per Table 3.21 the experimental & calculated values of adsorption capacity are not in good agreement. From the figure 3.18, the obtained correlation coefficient value i.e. R² is 0.13 & it is indicates very poor reaction. From all the above mentioned evidences it was observed that the phenol removal by ASMA did not follow pseudo first order kinetic model.

2) Pseudo-Second Order Model

\[
t / q_t = 1 / k_2 q_e^2 + (1 / q_e) t
\]

Where, \( k_2 \) is the pseudo-second order rate constant (g mg⁻¹ min⁻¹) \(^{[50]}\). The value of \( q_e \) is determined from the slope of the plot of \( t / q_t \) versus \( t \) (figure 3.21). The experimental value of \( q_e \) (1.1 mg/gm) from the pseudo second order model & it is in good agreement with calculated \( q_e \) value (0.94 mg/gm). More over from the figure 3.21, the obtained value of correlation coefficient i.e. \( R^2 = 0.9 \) indicates good reaction. This suggests that the rate of reaction system pseudo second order kinetic model. The value of kinetic constants and \( q_e \) values of Phenol sorption onto ASMA are given in table 3.23.
Table 3.22: Pseudo-Second Order Kinetic

<table>
<thead>
<tr>
<th>Time Interval (min.)</th>
<th>t/qt</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>30 / 0.36 = 83.33</td>
</tr>
<tr>
<td>60</td>
<td>60 / 0.71 = 42.25</td>
</tr>
<tr>
<td>90</td>
<td>90 / 0.94 = 31.91</td>
</tr>
</tbody>
</table>

Figure 3.21: Pseudo-Second Order Kinetic Study for Phenol Adsorption on ASMA

- Calculation from Graph

Qe (Calculated) = 1/Slope from graph = 1/-0.869 = -1.1

Intercept = 104.4 = 1/K₂qₑ²

i.e. K₂ = 1/ [104.4*(-1.1)²] = 0.008 gm/mg/minute
Table 3.23: Pseudo-Second Order Kinetic Parameters for Phenol Adsorption on ASMA

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>qₑ (mg/gm) (Exp.)</th>
<th>qₑ (mg/gm) (Cal.)</th>
<th>K₂ (g mg⁻¹ min⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASMA</td>
<td>0.94</td>
<td>-1.1</td>
<td>0.008</td>
<td>0.9</td>
</tr>
</tbody>
</table>

3) Intra-Particle Diffusion Model

The Pseudo First Order & Pseudo Second Order kinetic models could not identify the diffusion mechanism & the kinetic results were then analyzed by using intra-particle diffusion model. In the model developed by Weber & Morris, the initial rate of intra-particle diffusion is calculated by linearization of following equation.

\[ q_t = k_{id} t^{1/2} + C \]

Where, C is the intercept & k_{id} is the intra-particle diffusion rate constant. The intra-particle diffusion rate constant was determined from the slope of linear gradients of the plot qₜ versus \( t^{1/2} \) [50] as shown in the figure 3.22. The values of rate constant of intra-particle diffusion are given in table 3.25.

According to this model, the plot of uptake, qₜ, versus the square root of time (\( t^{1/2} \)) should be linear if intra-particle diffusion is involved in the adsorption process & if this line pass through the origin then intra-particle diffusion is the rate controlling step [58]. When the plot does not pass through the origin, this is indicative of some degree of boundary layer control & this further show that intra-particle diffusion is not only rate-limiting step, but also other kinetic models may control the rate of reaction, all of which may be operating simultaneously [59]. From the figure 3.22 it is clear that the linear line of the graph is not passing from the origin. This indicates that intra-particle diffusion is not only rate-limiting step. But the graph is linear & it indicates that the intra-particle diffusion is involved in the process. The value of intercept C (from graph) & experimental values of adsorption capacity (qₑ, mg/gm) are not in good agreement.

[167]
Table 3.24: Parameters of Intra-Particle Diffusion

<table>
<thead>
<tr>
<th>Time Interval (min.)</th>
<th>qt (mg/gm)</th>
<th>√Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.36</td>
<td>5.5</td>
</tr>
<tr>
<td>60</td>
<td>0.71</td>
<td>7.7</td>
</tr>
<tr>
<td>90</td>
<td>0.94</td>
<td>9.5</td>
</tr>
</tbody>
</table>

Figure 3.22: Intra-Particle Diffusion Study for Phenol Removal from Aqueous Solution

Table 3.25: Intra-Particle Diffusion Parameters from Graph

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>K_{id}</th>
<th>C (graph)</th>
<th>q_e (exp.) (mg/gm)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASMA</td>
<td>0.1455</td>
<td>-0.4311</td>
<td>0.94</td>
<td>0.9</td>
</tr>
</tbody>
</table>
3.3.3 Adsorption Isotherm Studies

1. Langmuir Isotherm

The experimental result of Langmuir isotherm for uptake of Phenol (Ini. Conc. 61 mg/L) on ASMA from Aqueous Solution is shown in table 3.26 & Langmuir constant calculated from graph is shown in table 3.27. Graphical representation of the same is shown in figure 3.23.

Table 3.26: Langmuir Isotherm Data for Uptake of Phenol (Ini. Conc. 61 mg/L) on ASMA from Aqueous Solution.

<table>
<thead>
<tr>
<th>Adsorbent Dosage (gm)</th>
<th>Langmuir Isotherm</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce (Final Conc. of Adsorbate) (mg/L)</td>
<td>qe (Adsorption Capacity) (mg/gm)</td>
</tr>
<tr>
<td>12</td>
<td>21</td>
<td>1.6</td>
</tr>
<tr>
<td>24</td>
<td>28</td>
<td>2.75</td>
</tr>
<tr>
<td>36</td>
<td>9</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 3.23: Langmuir Isotherm Plot for Uptake of Phenol on ASMA from Aqueous Solution

Calculation from Graph:

Langmuir Equation: \( \frac{Ce}{qe} = \frac{1}{Q_0} b + \frac{1}{Q_0} \times C_e \)

\( Q_0 = \frac{1}{\text{Slope}} = \frac{1}{0.49} = 2.04 \text{ mg/gm; } b = \text{Intercept} \times Q_0 = 2.30 \times 2.04 = 4.7 \text{ (L/mg)} \)
Table 3.27: Langmuir Constants for Uptake of Phenol on ASMA from Aqueous Solution

<table>
<thead>
<tr>
<th>Q₀ (mg/gm)</th>
<th>b (L/mg)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.04</td>
<td>4.7</td>
<td>0.71</td>
</tr>
</tbody>
</table>

The values of coefficient of correlation (R²) for uptake of Phenol on ASMA obtained is in good agreement. The value of R² is 0.71, which is nearer to 1, indicates favorable adsorption. It indicates first layer of molecules adhere to the surface with energy comparable to heat of adsorption for monolayer sorption and subsequent layers have equal energies \(^{54, 60}\). Here we can say that Langmuir isotherm applies to each layer \(^{60, 61}\). The higher values of Q₀ i.e. 100 mg/gm & b i.e. 4.7 obtained for uptake of Phenol on ASMA for Langmuir isotherm suggest better applicability of it. Thus uptake of Phenol on ASMA has good fit for Langmuir isotherm.

2. Freundlich Isotherm

Results of modeling of the isotherms of Phenol adsorption by ASMA according to Freundlich isotherm model is summarized in table 3.28. Graphical presentation of the Freundlich isotherm is represented in figure 3.24. Table 3.29 shows the Freundlich constants calculated from graph.

Table 3.28: Freundlich Isotherm Values for Uptake of Phenol (Ini. Conc. 61 mg/L) on ASMA from Aqueous Solution.

<table>
<thead>
<tr>
<th>Adsorbent Dosage (gm)</th>
<th>Freundlich Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce (Final Conc. Of Adsorbate) (mg/L)</td>
</tr>
<tr>
<td>12</td>
<td>21</td>
</tr>
<tr>
<td>24</td>
<td>28</td>
</tr>
<tr>
<td>36</td>
<td>9</td>
</tr>
</tbody>
</table>
Calculation from Graph:

Freundlich Equation: \( \log_{10} q_e = \log_{10}(K_f) + \frac{1}{n} \log_{10}(C_e) \)

\[ n = \frac{1}{\text{Slope}} = \frac{1}{0.56} = 1.8 \text{ L/mg} \]

\[ K_f = \text{Antilog (Intercept)} = \text{Antilog (0.38)} = 2.4 \]

Table 3.29: Freundlich Constants for Uptake of Phenol (Ini. Conc. 61 mg/L) on ASMA from Aqueous Solution.

<table>
<thead>
<tr>
<th>( K_f ) (mg/gm)</th>
<th>( n ) (L/gm)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4</td>
<td>1.8</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Here the value of \( K_f \) i.e. adsorption capacity 2.4 mg/gm & adsorption intensity \( n \) (rate of adsorption) & i.e. 1.8 L/gm is obtained from Freundlich isotherm. The value of \( n \) fulfills the condition \( (0 < n < 1) \) of Freundlich isotherm \(^{[50, 51, 60]} \). The value of \( n \) in the range 2-10 represent good, 1-2 moderately difficult and less than 1 poor adsorption characteristics \(^{[62]} \). Here the value of intensity i.e. is 1.8 which is almost 2 represents moderately difficult adsorption characteristics. The value of coefficient of correlation \( (R^2) \) for uptake of Phenol on ASMA obtained is in good agreement. The value of \( R^2 \) is 0.6 indicates good adsorption.
The data obtained from the Freundlich plot indicates that the adsorption sites are not identical; the total adsorbed amount is the same over all types of sites. It encompasses the heterogeneity of the surface, exponential distribution of sites and their energies. It reflects van der walls adsorption in the middle concentration range [63].

3. Temkin Isotherm

Results of modeling of the isotherms of Phenol adsorption by ASMA according to Temkin isotherm model is summarized in table 3.30. Graphical presentation of the Temkin isotherm is represented in figure 3.25. Table 3.31 shows the Temkin constants calculated from graph.

Table 3.30: Temkin Isotherm Values for Uptake of Phenol (Ini. Conc. 61 mg/L) on ASMA from Aqueous Solution.

<table>
<thead>
<tr>
<th>Adsorbent Dosage (gm)</th>
<th>Temkin Isotherm</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce</td>
<td>ln C</td>
<td>X (mg/gm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Final Conc. Of Adsorbate) (mg/L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>41</td>
<td>3.7136</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>28</td>
<td>3.3322</td>
<td>2.75</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>9</td>
<td>2.1972</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.25: Temkin Isotherm Plot for Uptake of Phenol on ASMA from Aqueous Solution
Table 3.31: Temkin Constants for Uptake of Phenol on ASMA from Aqueous Solution

<table>
<thead>
<tr>
<th>a (mg/gm)</th>
<th>b (L/mg)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.24</td>
<td>0.66</td>
<td>0.34</td>
</tr>
</tbody>
</table>

The value of correlation coefficient $R^2$ is 0.34 indicates poor adsorption characteristic with Temkin isotherm. The Temkin isotherm does not fit the present study.

4. BET Isotherm

Results of modeling of the isotherms of Phenol adsorption by ASMA according to BET isotherm model is summarized in table 3.32. Graphical presentation of the BET isotherm is represented in figure 3.26. Table 3.33 shows the BET constants calculated from graph.

Table 3.32: BET Isotherm Values for Uptake of Phenol (Ini. Conc. 61 mg/L) on ASMA from Aqueous Solution.

<table>
<thead>
<tr>
<th>Adsorbent Dosage (gm)</th>
<th>BET Isotherm</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_f$ (Final Conc. of Adsorbate) (mg/L)</td>
<td>$q$ (mg/gm)</td>
<td>$C_f/C_s$</td>
<td>$C_f/(C_s - C_f)q$</td>
</tr>
<tr>
<td>12</td>
<td>41</td>
<td>1.6</td>
<td>0.67</td>
<td>3.28</td>
</tr>
<tr>
<td>24</td>
<td>28</td>
<td>2.75</td>
<td>0.46</td>
<td>2.33</td>
</tr>
<tr>
<td>36</td>
<td>9</td>
<td>1</td>
<td>0.15</td>
<td>0.17</td>
</tr>
</tbody>
</table>
Figure 3.26: BET Isotherm Plot for Uptake of Phenol on ASMA from Aqueous Solution

Calculation from Graph:

BET Equation: $\frac{C_f}{(C_s-C_f)}q = \frac{1}{Bq_{\text{max}}} - \frac{(B-1)}{Bq_{\text{max}}} \left( \frac{C_f}{C_s} \right)$

$\frac{1}{Bq_{\text{max}}} =$ Intercept i.e. $Bq_{\text{max}} = -1.6$ i.e. $q_{\text{max}} = -1.6 / -8.6 = 0.2$ mg/gm

$\left( \frac{(B-1)}{Bq_{\text{max}}} \right) =$ Slope = 6.00 i.e. $B - 1 = 6 \times -1.6$ i.e. $B = 8.6$ (L/mg)

Table 3.33: BET Constants for Uptake of Phenol on ASMA from Aqueous Solution

<table>
<thead>
<tr>
<th>$q_{\text{max}}$ (mg/gm)</th>
<th>B (L/mg)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>-8.6</td>
<td>0.99</td>
</tr>
</tbody>
</table>

The experimental data for uptake of Phenol on ASMA have best fit for BET isotherms of adsorption isotherm. The value of $R^2$ obtained 0.99 for BET isotherm indicates the same. Here we can say that BET isotherm as an extension of the Langmuir isotherm to account for multilayer adsorption and Langmuir isotherm applies to each layer.\[61\]
3.4 Regeneration Study

After removal of Phenol from Waste Water, ASMA can be regenerated using Acetone by following method.

- 4 gm of exhausted ASMA (i.e. ASMA after Phenol adsorption) was taken in a beaker.
- 20 to 25 ml of Acetone was added in it.
- The beaker was kept on the magnetic stirrer for 1 Hr at 24°C. The mixture was shaken well.
- Arrange the distillation assembly. Take the above mixture in round bottom flask.
- Then after collect the distillate of a mixture of Acetone & Phenol in a distillation flask.
- Here, boiling points of Acetone & Phenol are 56°C & 181.7°C respectively.
- Therefore, conduct distillation process at 56°C & distilled out the Acetone in a collection beaker.
- Collect the distillate of Acetone & store it in a glass bottle.
- This Acetone can be used further in various processes.
- The remaining Phenol, in a distillation flask, was tested to measure the concentration of Phenol desorbed from the ASMA & extracted in Acetone.
- After completion of distillation, Phenol crystals were observed in the distillation flask.
- The distillation flask was washed with little water to collect the Phenol.
- 2 ml of washed content was taken to measure the concentration of Phenol.
- The final concentration of Phenol was measured by using above mentioned 4-Amino Antipyrine Method without Chloroform Extraction Method.
- From the result we found 25.6 mg/L concentration of extracted Phenol. The initial high concentration of Phenol was 70 mg/L & after adsolubilization by 4 gm/100 ml ASMA it was 20 mg/L.
- That means 50 mg/L of Phenol was adsolubilized on ASMA.
- During Acetone treatment almost 25.6 mg/L of Phenol desorbed from the ASMA & extracted in the Acetone.
- From the results shown in the table 3.34 almost 51.2% Phenol was recovered.
- To get maximum recovery of Phenol from exhausted ASMA, re-extraction was carried out with Acetone in the same manner as mentioned above.
- The final conc. Of recovered Phenol was measured 23.5 mg/L

[175]
• From the results shown in table 3.34 almost 96.3% Phenol can be recovered after re-
  extraction of Phenol by Acetone.
• Regenerated ASMA can further be used in the treatment whereas extracted Phenol 
can be reused in the industry as raw material.

Table 3.34: Recovery of Phenol

<table>
<thead>
<tr>
<th>Initial Conc. Of Phenol (mg/L)</th>
<th>Final Conc. of Phenol (mg/L)</th>
<th>Quantity of Exhausted ASMA (gm)</th>
<th>Quantity of Acetone (ml)</th>
<th>Contact Time for Recovery (Hr.)</th>
<th>Temp. (°C)</th>
<th>Conc. of Phenol Adsolubilized on ASMA (mg/L)</th>
<th>Conc. of Phenol Extracted by Acetone (mg/L)</th>
<th>% Recovery of Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Extraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>20</td>
<td>4</td>
<td>20</td>
<td>1</td>
<td>24</td>
<td>25.6</td>
<td></td>
<td>51.2</td>
</tr>
<tr>
<td>2nd Extraction (The residues remain after 1st extraction was retreated)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>4</td>
<td>20</td>
<td>1</td>
<td>24</td>
<td>50 – 25.6 = 24.4</td>
<td></td>
<td>23.5</td>
</tr>
</tbody>
</table>

3.5 Removal of Phenol from the Wastewater Sample of Pharmaceutical Industry

To check the effectiveness of the treatment given to the synthetic sample (as described earlier) the experiment was again performed on actual sample of Pharmaceutical Industry. As the sample was turbid it was simply digested first to get clear sample & whole removal treatment was carried out on the same sample. pH, contact time & adsorbent dosage were adjusted 4, 1.5 hr & 40 gm/L respectively (equilibrium from experiment 3.11.1, 3.11.2 & 3.11.3 respectively). Maximum 68% removal of Phenol form actual industrial sample by ASMA was observed where as it was 70 - 80% for synthetic sample. The results of % removal have been mentioned in Table 3.35. From the results it was observed that the ASMA is an effective adsorbent to remove organic pollutant like Phenol from industrial waste water. It may remove more than 68 % of Phenol from the Aqueous Solution if the sample would be treated again with fresh adsorbent ASMA.

[176]
Table 3.35: % Removal of Phenol from Actual Sample

<table>
<thead>
<tr>
<th>Equilibrium Adsorbent Dosage (Gm/L)</th>
<th>Equilibrium Contact Time (Hr)</th>
<th>Equilibrium pH</th>
<th>High Initial conc. of Phenol (mg/L)</th>
<th>Absorbance</th>
<th>Final Conc. of Phenol from Calibration Curve (mg/L)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1.5</td>
<td>4</td>
<td>14.2</td>
<td>0.064</td>
<td>4.6</td>
<td>68</td>
</tr>
</tbody>
</table>

3.6 Conclusion

From the batch experiment studies it was observed that the Anionic Surfactant Modified Alumina can be used as an adsorbent in the waste water treatment for the removal of Phenol – an organic pollutant. This chapter includes potential of Anionic Surfactant Modified Alumina, prepared earlier, in removal of Phenol from aqueous solution as well as from actual industrial samples. The variables for pH were decided 2, 4, 6, 8 & 10 to find out optimum pH for further treatment. While studying pH variables; other parameters such as high initial concentration of Phenol (61 ppm), Contact Time (1.5 Hr), & Adsorbent ASMA Dosage (12 gm/L) were kept constant. The variables for contact time were decided as 1/2 Hr, 1 Hr, 1.5 Hr & 2 Hr to find out optimum contact time for further treatment. While studying Contact Time variables; other parameters such as high initial concentration of Phenol (61 ppm), pH (4 – optimum pH obtained from previous study), & Adsorbent ASMA Dosage (12 gm/L) were kept constant. The variables for Adsorbent ASMA Dosage were decided as 12 gm/L, 25 gm/L & 40 gm/L to find out optimum adsorbent dosage for further study. While studying Adsorbent ASMA Dosage variables; other parameters such as high initial concentration of Phenol (61 ppm), pH (4 – optimum pH obtained from previous study) & Contact Time (1.5 Hr – optimum contact time obtained from Previous study) were kept constant. The variables for adsorbate concentration were decided as 50 ppm & 70 ppm to find out optimum adsorbate concentration for further study. While studying high intial Adsorbate Concentration variables; other parameters such as pH (4 – optimum pH obtained from previous study) & Contact Time (1.5 Hr – optimum contact time obtained from previous study) & Adsorbent ASMA Dosage (40 gm/L – optimum contact time obtained from previous study) were kept constant. From the batch study; pH 4 (18.7% removal of Phenol), contact time 1.5 Hr (18.5% removal of Phenol) & adsorbent dosage 40 gm/L (66% removal of Phenol) were found optimum experimental conditions for removal of Phenol from aqueous solution. From the
adsorbate variable study it was observed that different adsorbate concentration did not affect Phenol removal by ASMA from aqueous solution. It showed 70% removal of Phenol for all the adsorbate concentrations. It shows that the ASMA can be used to remove Phenol of any high range. Study on effect of temperature was also carried out to observe the removal of Phenol by ASMA from aqueous solution. The variables for temperature were decided as 30 °C, 40 °C & 50 °C to find out optimum temperature range. It was observed that temperature had no effect on Phenol removal. It showed 70% removal of Phenol by ASMA for all the temperature range. From the chemical kinetic study it was observed that the rate of reaction of Phenol removal followed Pseudo Second Order Kinetic Model. The calculated qe value (0.94 mg/gm) from the Pseudo Second Order Kinetic Model & it was in good agreement with experimental value of qe (1.1 mg/gm) for the same. Correlation coefficient value i.e. \( R^2 = 0.9 \) for Pseudo Second Order Kinetic Model indicated good rate of reaction. The values of coefficient of correlation (\( R^2 \)) for adsorbent ASMA obtained were in good agreement with Langmuir (\( R^2 = 0.71 \)), Freundlich (\( R^2 = 0.6 \)) & BET (\( R^2 = 0.99 \)) isotherms.

For the regeneration of ASMA, Acetone was used. In this study it was found that only Phenol was desorbed from the ASMA & not surfactant. This is due to pH is less than \( Z_{pc} \) of Alumina i.e. 9.15. During recovery, 4 gm of exhausted ASMA was treated with 20 ml of Acetone for 1 Hr. at 24 °C. Almost 50% recovery of Phenol was observed during 1st extraction. The recovery was extended to get maximum recovery & we have obtained maximum 96.3% recovery of Phenol.

As shown previously the removal efficiency was also checked on actual industrial sample & 68% phenol removal was found. From the study it is confirmed that ASMA is very good adsorbent & it can be efficiently used in industries to remove phenol from the effluent.
3.7 Recommendation

Industries may use this adsorbent ASMA in their treatment plant to remove organic pollutant like Phenol. These data can be used in designing and fabrication of an economic treatment plant for the removal of Phenol from wastewaters of various industries like pharmaceutical industry after conducting treatability study on the actual sample. By applying this technology we can prevent the introduction of Phenol into adjacent water resources like ground water & surface water.

Phenol is one of the most dangerous constituents of waste water of many industries like Polymer manufacturing, Dye manufacturing, Drug producing, etc. As they are easily soluble in water, they can damage public health by running to the drinking water discharge point. Anionic Surfactant Modified Alumina can adsolubilize phenol efficiently from aqueous media without consuming much energy. Again the Phenol can be regenerated by using Acetone – an organic solvent & both can be separated by distillation. Thus separated Acetone & Phenol can be re-used as raw materials again in the industries.
Probable Treatment Layout for the Removal of Phenol by using Anionic Surfactant Modified Alumina is given below in figure 3.27.

**Figure 3.27: Treatment Layout for the Removal of Phenol by using Anionic Surfactant Modified Alumina.**
3.8 Reference:

1. http://www.cliffsnotes.com/study_guide/Phenols.topicArticleId-23297, articleId-23262.html

2. WIKIPEDIA, Free Encyclopedia


14. Potential for Human Exposure, Page 149


20. Marrot et al., 2006; Bodalo et al., 2008; Jayachandran and Kunhi, 2008

21. Removal of Phenolic Compounds From Industrial Waste Water by SemifluidizedBed Bio-Reactor MR. B. C. MEIKAP Lecturer, Department of Chemical Engineering, Regional Engineering Collage, Rourkela - 769 008 (Orissa) & DR. G. K. ROT Professor & Head, Department of Chemical Engineering, R E. C. Rourkela-769 008


25. Chakraborty S., Bhattacharya T., Patel T., Tiwari K., Biodegradation Of Phenol By Native Microorganisms Isolated From Coke Processing Wastewater, Journal of
Environmental Biology ©Triveni Enterprises, Lucknow (India) (For personal use only Free paper downloaded from: www.jeb.co.in), 31, 293-296 (2010)


31. Hanscha, Corwin; McKarnsb, Susan C; Smith, Carr J; Doolittle, David J., Comparative QSAR evidence for a free-radical mechanism of phenol-induced toxicity, Chemico-Biological Interactions, 127 (1), 61–72, (2000) doi:10.1016/S0009-2797(00)00171-X. PMID 10903419

32. Brown V., Box V., Simpson B., Decontamination Procedures for Skin Exposed to Phenolic Substances, Archives of Environmental Health, 30 (1), 1–6, (1975) PMID 1109265


52. Noll K. E et al, Adsorption technology for the air and water pollution control, *Lewis Published Inc.*, (1992)


