1.1. PHENOLS

Phenol is an organic compound with the formula of C_6H_5OH. It is colorless, crystalline and is polar in nature which makes it water soluble.

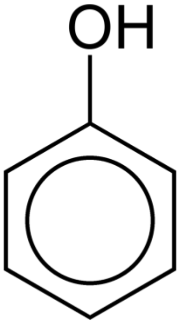

Fig 1.1.: Structure of phenol

1.1.1. PHYSICAL PROPERTIES OF PHENOL

Phenol is a white crystalline solid compound smelling of a disinfectant. The crystals are hygroscopic in nature and absorb water on exposure to atmosphere. The melting point of phenol is 43^0C. The boiling point is 182^0C. Phenol has a solubility of around 8 gm per 100 mL of water.

1.1.2. CHEMICAL PROPERTIES OF PHENOL

Aqueous solution of phenol is weakly acidic and turns blue litmus slightly to red. Phenol is easily neutralized by sodium hydroxide forming sodium phenate or phenolate. Phenol is highly reactive toward electrophilic aromatic substitution as the oxygen atom's pi electrons donate electron density into the ring. By this general approach, many groups can be appended to the ring, via halogenation, acylation, sulfonation, and other processes.

1.1.3. ADVERSE EFFECTS OF PHENOL

Phenol and its derivatives cause irritation in eyes and skin. The inhalation of these vapours can cause damage to the respiratory tract. Phenols are also carcinogenic and capable of causing damage to DNA. On long term use, phenol causes damage to liver and kidneys. On prolonged exposure to skin it causes dermatitis.

Phenol is mainly used in the chemical production of Cresols, Alkyl phenols, Tylenols, Phenol resins, Aniline and other compounds. It is used in pesticides, in explosives, in dyes and in textile industries. (Michałowicz, et al, 2007) Thus it forms a major part of the effluents of these industries. The concentration of phenol and its derivatives on an average in various effluents are Petrochemicals: 3.9 mg/L - 1230 mg/L, Coking operations: 29 mg/L - 3950 mg/L, Paper industries: 0.2 mg/L – 1700 mg/L, Coal processing: 10 mg/L-6900 mg/L and Refineries: 5 mg/L- 600 mg/L (Farhod Chasib, et al, 2013).

Apart from these, Phenols may be released into environment due to natural processes like decomposition of organic matter and synthesis of various phenols by fungi and a few plants. The various derivatives of Phenol present in these effluents are: Chlorophenols, Catechols, Chlorocatechols, Nitrophenols, Methyl phenol and other Alkyl phenols, Bisphenols, Aminophenols, Butylhydroxytoluene and Butylhydroxyanisole. These phenols are toxic to humans as well as other organisms. In humans it results in respiratory irritation, headache, burning eyes (on short term exposure by inhalation), high concentrations of phenols result in anorexia, fatigue, damage to kidney and liver, paralysis and death in severe cases. Hence it becomes important for the industries to treat their effluents to make sure that the phenols are present in acceptable concentrations in their waste water in order to avoid their toxicity to various living organisms.

1.2. METHODS FOR REMOVAL OF PHENOLS FROM WASTE WATER

Various methods have been used for the removal or recovery of phenols from waste water. These methods can broadly be classified as physical, chemical and biological methods.

1.2.1. PHYSICAL METHODS

The physical methods for the removal of phenol involve the physical separation of phenol from the mixture of compounds. The different techniques used for this separation of phenol are pervaporation, adsorption, adsorption-flocculation, electro-flocculation and electrochemical treatment.

1.2.1.1. PERVAPORATION

Pervaporation is a selective membrane process. It is one of the widely used techniques for the separation of components of liquid-liquid mixtures by partial vaporization through porous or non porous membranes. It can be used for the removal of phenol.(Kujawski et al., 2004). Composite membranes such as PERVAP-1060, PERVAP-1070 and PEBA can be used. PEBA was found to have the best removal efficiency of phenol.

1.2.1.2. MEMBRANE BASED SOLVENT EXTRACTION

Solvent extraction is a common industrially used equilibrium-based separation process. Membrane solvent extraction can be used for the treatment of phenol in the effluents by cumene oxidation process. (Lazarova et al.,2004)The membrane based experiments have been carried out using a membrane cross-flow type contractor which was provided with hollow-fiber hydrophobic membranes Celgard X-30. Extraction solvents like Methyl-ter-butyl ether (MTBE), cumene and a mixture of hydrocarbons have been used for this process.

1.2.1.3. ADSORPTION- FLOCCULATION

Phenol can be removed from waste water by adsorption-flocculation using organobentonite (Shen et al., 2002). The study examined the feasibility of using bentonite modified by the addition of the small cationic surfactant to remove phenol from water. Bentonite used contained 3.6% sand, 7.3% silt, and 89.1% clay. 90% phenol was removed and almost 100% bentonite was recovered.

1.2.1.4. ELECTRO CHEMICAL TREATMENT

Direct electrolysis can be used for the oxidation of phenolic compounds. These methods involve the passage of electricity through a solution of waste water containing the oxidizable phenolic compounds (Comninellis et al.,1991) by changing the anode material the efficiency obtained can be varied. Ti/Pt anodes are considered to have the highest electrocatalytic activity. The efficiency of the process can be increased by increasing the chloride concentration in the water which results in an increase in the COD of the water thus increasing the susceptibility of compounds towards oxidation. The set up requires huge investments and maintenance costs which makes it unaffordable to the small scale industries.

1.2.1.5. REVERSE OSMOSIS

RO method can be used to efficiently remove the phenols from waste waters. An efficiency of almost 99% has been achieved. (Kurihara et al., 1981) listed several organic rejections of the Toray composite membrane PEC-1000 (polyfuran); most rejections were high. A composite membrane can be used for removal of various phenols and their derivatives. (Koyama et al., 1982).

1.2.2. CHEMICAL METHODS

1.2.2.1. EXTRACTION

Extraction is the process of transferring a particular solute from a mixture of solutes in the feed solution into a particular immiscible phase i.e. the solvent phase. Acetone is the most commonly used solvent for the extraction of phenol (Mahugo Santana et al., 2009). Extraction is a very costly process. But the costs can be reduced by the recovery and reuse of the solvent. Current standard methods of phenolic compounds analysis in water samples are based on liquid–liquid extraction (LLE) while Soxhlet extraction is the most used technique for isolating phenols from solid phases. These methods are being replaced by methodologies such as solid-phase extraction (SPE) and solid-phase microextraction (SPME) which have increased the efficiency of the extraction process. Along with these there are also resins such as Amberlite^{TM} being used for high efficiency recovery of the phenols and the organic solvents.

1.2.3. BIOLOGICAL METHODS

The biological methods mainly utilize the metabolisms of the cells and the enzymes involved to degrade the phenolic compounds. These methods are considered to be the safest methods since they are biodegradable and also detoxify phenols. There are two main types of biological methods utilized under biological methods. i.e. microbial degradation and enzymatic polymerization.

1.2.3.1. ENZYMATIC POLYMERIZATION

Enzymes catalyze specific reactions and mostly act under moderate conditions (temperature, pH, solvents and ionic strength). Hence enzymes represent a promising tool for the selective removal of pollutants from waste streams. Enzyme-based processes act with high specificity and are very efficient in removing targeted compounds. Peroxidases are the most widely reported enzymes for phenol polymerization when compared with other enzymes.

1.2.3.2. MICROBIAL DEGRADATION

Microbial degradation is a useful strategy to eliminate organic compounds and detoxify wastewaters and polluted environments (Kobayashi et al., 1982). Phenol is degraded by diverse microorganisms including yeasts, fungi and bacteria Because of widespread occurrence of phenol in the environment, many microorganisms utilize phenol as the sole carbon and energy source which includes both aerobic and anaerobic microorganisms. Various microorganisms used for detoxification of phenol are: Aspergillus sp., Bacillus brevis, B. subtilis, Rhodococcus erythropolis, Staphylococcus sp., Candida tropicalis, Trichosporon cutaneum, Pseudomonas etc. (Pradeep et al., 2014).

1.3. ADSORPTION

The phenomenon of accumulation of molecules (liquid or gas) on any surface due to physical or chemical forces of attraction is called as adsorption. The most common forces responsible for adsorption are Vander wall's forces of attraction, Hydrogen bonding, Ionic bonding, Metallic bonding and covalent forces of attraction. These bonds can be either reversible or irreversible. There are two types of adsorption: Physisorption and Chemisorption. If the forces are weak and the adsorption can be reversed, then it is called as physisorption. If there are chemical bonds formed and the process is irreversible, then it is called as chemisorption.

While absorption is a bulk phenomenon, adsorption is a surface phenomenon and the molecules can be easily recovered.

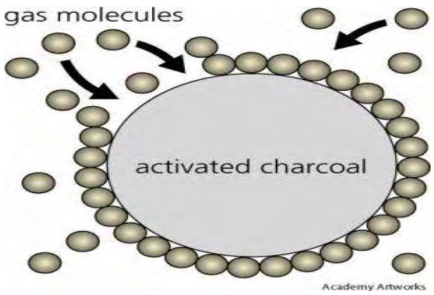

Fig 1.2. Adsorption mechanism

1.4. ADSORPTION IN THE REMOVAL OF PHENOLS FROM WASTE WATER

Adsorption on activated carbon is currently being used and is most effective in treating high strength and low volume of phenol wastewater. (Girish et al., 2014). Activated carbon is the most widely used adsorbent for the removal of a variety of phenols from wastewater. Activated carbon can be produced from any carbonaceous solid precursor: Both naturally occurring and synthetic. The selection of the precursor essentially determines the range of adsorptive and physical properties that can be attained in the activated carbon products. But the disadvantage associated with it is its high cost due to the use of non-renewable and relatively expensive starting material such as coal, which is a major economic consideration. This has prompted a growing research interest in the production of activated carbons from locally available materials especially for application concerning wastewater treatment. Several agricultural byproducts have been found to be suitable precursors for production of activated carbon. Because the biomass obtained from these materials are cheaper, renewable and abundantly available and have high carbon and low ash content. So agricultural wastes can be used as adsorbents for the removal of phenol.

Table 1.1: Differences between Physisorption and Chemisorption

PHYSISORPTION	**CHEMISORPTION**
Weak Vander Waal's forces are responsi for Physisorption.	The forces responsible for chemisorption are coval bonds.
The heat of adsorption is low i.e. about 20 – 40 kJ mol^{-1}	The heat of adsorption is high i.e. about 40 – 400 mol^{-1}
There are no compounds formed.	Surface compounds are formed.
The process is reversible	The process is irreversible.
It does not require any activation energy.	It requires activation energy.
Decreases with increase of temperature.	First increases with increase of temperature and t decreases.
It is not specific in nature	It is specific in nature and occurs only when there some possibility of compound formation
It results in the formation of a multimolecul Layer	It results in a unimolecular layer.

1.5. ADSORPTION ISOTHERMS:

Adsoption isotherms are mathematical and graphical models used to study the nature of adsoption and predict the nature of adsoption. The most common types of isotherms are: linear isotherm, Freundlich isotherm, Langmuir isotherm, Fick's isotherm (Y.S. Ho., et al, 2001).

1.5.1. LINEAR ISOTHERM:

In this isotherm, the amount of adsorbate adsorbed per unit surface area of the adsorbent is directly proportional to the concentration of adsorbate in the solution.

1.5.2. LANGMUIR ISOTHERM:

Langmuir isotherm is represented by the equation:

$$1/q_e = (1/q_L K_L C_e) + (1/q_L) \text{ ------------- } (1.1)$$

Where

q_e is maximum amount of adsorbate adsorbed in equilibrium per gram of adsorbent (mg/g)

q_L is maximum monolayer coverage capacity (mg/g)

K_L is Langmuir isotherm constant (L/mg)

C_e is equilibrium concentration of adsorbate (mg/L)

A Langmuir isotherm gives a curve if a graph is plotted between the concentration of adsorbate as y axis and the q value as X axis. Where q is given by,

$$q= ((Cf-Ci) *V)/ m \text{ ------------- } (1.2)$$

Or

q = ((final concentration of adsorbate – initial concentration of adsorbate)/ mass of adsorbent used)* Volume of solution prepared.

In order to confirm the Adsorption following Langmuir isotherm, a graph between ln q and ln C is plotted. This graph gives a straight line passing through the origin.

1.5.3. FREUNDLICH ISOTHERM:

$qe = KF (Ce)^{1/n}$ ------------- (1.3)

Where,

KF is the Freundlich isotherm constant.

n is the adsorption intensity

1.5.4. SIP'S ISOTHERM:

$q_e = K_{LF}Ce^{nLF}/(1 + (a_{LF}C_e)^{nLF})$ -------------- (1.4)

K_{LF} is Sip's isotherm constant.

1.5.5. DUBININ – RADUSHKEVICH:

$\ln qe = \ln qm - ß\, \epsilon^2$ ---------------- (1.5)

1.5.6. TEMKIN ISOTHERM:

$qe = B \ln A + B \ln Ce$ ------------- (1.6)

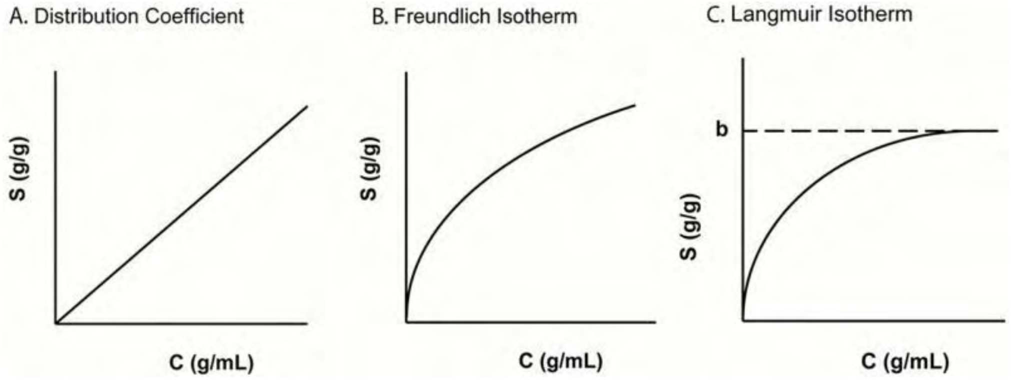

Fig 1.3: Graphs of Different isotherm

1.6. ZEA MAYS AS AN AGRICULTURAL ADSORBENT

Zea Mays is one of the best alternatives available for activated carbon. Zea mays wastes are easily available and since are biodegradable, they can be easily disposed off. Along with this, Zea mays can also detoxify the Phenols due to the presence of Peroxidase and polyphenol oxidase enzymes and hence reduces the problems of adsorbate disposal. Zea mays wastes can be used in the treatment of a wide range of toxic phenols present in the waste waters of many different industries like: Fertilizer industries, Petrochemical industries, Textile industries, Dyeing industries etc. Hence Zea mays wastes have a potential for becoming the future adsorbents in the line of effluent treatment.

1.7. OBJECTIVES OF THE STUDY:

1. To characterize different phenols and to plot standard curves for them.
2. To conduct qualitative and quantitative analysis of industrial waste water for the presence of phenol.
3. To conduct batch adsorption kinetic studies for the removal of phenol using waste parts of Zea Mays as adsorbent.
4. Fitting isotherms for batch kinetic studies.