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Review on Removal of Phenol from Wastewater Using Low Cost Adsorbent

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***Abstract*— Phenol is a major pollutant in the wastewater because of its presence in the effluent of petroleum refining, coal conversion, plastics, textiles, iron and steel manufacturing as well as pulp and paper manufacturing. It is very important to remove phenol from contaminated water before discharge into any natural water because of their toxicity to aquatic organisms. It has severe effect on human being, both short term and long term. The methods such as adsorption, polymerization, electrocoagulation, extraction, photodecomposition, advanced oxidation and ion exchange are used for removal of phenol from waste water. Among them, physical adsorption method is generally considered to be the best, effective, low-cost and most frequently used method for the removal of phenolic pollutions. This method is suitable for phenol removal can be selected based on availability of the material, extent of separation required and properties of phenolic effluent.**

Locally available sawdust, easily and abundantly available material is tested experimentally as an adsorbent, after carbonization, for the removal of phenol from industrial waste waters for a safe disposal. The experiments are performed batch wise to remove phenol from synthesized aqueous solutions. The aim of the present work is to investigate the capability of sawdust used as an adsorbent for removal of phenol from wastewater and to study the effects of initial phenol concentration, adsorbent dosage, pH value and contact time on the adsorption process, then workout optimum conditions for removal. The efficiency of adsorbents is described and correlated with the usual Langmuir and Freundlich isotherm equations.

***Index Term*- Adsorption, Langmuir and Freundlich, Phenol, Removal.**

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I. INTRODUCTION

INDUSTRIAL effluents, major source of various kinds of pollution in natural water. Phenolic compounds which are generated from petroleum and petrochemical, coal conversion, and Phenol-producing industries are common contaminants in wastewater and suspected as toxic and carcinogenic. It is very important to remove phenol from contaminated water before discharge into any natural water because of their toxicity to aquatic organisms. It has severe effect on human being, both short term and long term. Various treatment technologies such as adsorption, photodegradation, flocculation, chemical oxidation, biological process, etc. are available for the removal of phenol from the wastewater. Among them adsorption is widely used for the removal of phenol from wastewater.

The toxic levels usually range between the concentrations of 10-24 mg/L for human and the toxicity level for fish between 9-25 mg/L. Lethal blood concentration of phenol is around 150-mg/100 ml. Due to the toxic nature of phenol several regulatory bodies all over the globe like the Ministry of Environment and Forests (MOEF), Government of India and EPA, USEPA have listed phenol and phenolic compounds on the priority-pollutants list as well as also have proposed maximum permissible limits of phenol in different categories of water. Maximum permissible limits if phenol in water is given in Table I.

TABLE I
MAXIMUM PERMISSIBLE LIMITS OF PHENOL IN WATER

Agency	Type of Water	Maximum Permissible limit
USEPA	Waste Water	0.1 PPM
BIS	Drinking Water	1.00 PPM
WHO	Drinking Water	1.00 PPM
MoEF	Industrial Effluent	1.00 PPM

The amount of phenol present in various industrial effluents which is given in table II,

TABLE II
AMOUNT OF PHENOL PRESENT IN VARIOUS INDUSTRIAL EFFLUENTS

Industry	Amount of phenol
Refineries	6-500 PPM
Coking	28-3900 PPM
Petrochemicals Manufacturing	2.8-1220 PPM
Coal Processing	9-6800 PPM

The aim of the present work is the test of adsorption in removing phenol from aqueous solution by adsorption onto treated sawdust as adsorbent. The influence of several parameters, such as pH, temperature, and initial concentration of phenol and contact time, on the adsorption process are investigated.

II. PHENOLS.

Phenols, sometimes called phenolics, are a class of aromatic organic compounds consisting of one or more hydroxyl groups attached to an aromatic hydrocarbon group. Phenol is a benzene derivative and is the simplest member of the phenolic chemical. Its chemical formula is C_6H_5OH and its structure is that of a hydroxyl group (-OH) bonded to a phenyl ring. Phenol is produced naturally and synthesized as a manufactured chemical. Naturally, it is a constituent of coal tar and creosote, decomposing organic material, human and animal wastes, and as a compound found in many non-foods and foods. Phenol is usually sold commercially as a thick liquid. The table III shows the physical properties of phenol.

TABLE III
PROPERTIES OF PHENOL

Property	Values
Molecular Weight (g/mol)	94.144
Molar Volume(cm^3/mol)	90
Boiling Point (^{0}C)	182
Melting point (^{0}C)	43
Auto ignitition temperature (^{0}C)	715

III. ADSORPTION PHENOMENON

Adsorption is a surface phenomenon with common mechanism for organic and inorganic pollutants removal. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, liquid–solid intermolecular forces of attraction cause some of the solute molecules from the solution to be concentrated or deposited at the solid surface. The solute retained (on the solid surface) in adsorption processes is called adsorbate, whereas, the solid on which it is retained is called as an adsorbent. This surface accumulation of adsorbate on adsorbent is called adsorption. This creation of an adsorbed phase having a composition different from that of the bulk fluid phase forms the basis of separation by adsorption technology. As the adsorption progress, equilibrium of adsorption of the solute between the solution and adsorbent is attained. The phenomenon of the enrichment of chemical substances at the surface of a solid is called adsorption. All adsorption performance processes are depends on solid-liquid equilibria and on mass transfer rates. The adsorption operation can be batch, semi-batch and continuous. The adsorption amount of the molecules at the equilibrium step was determined according to the following equation:

$$qe = V\,(Co\text{-}Ce)\,/M$$

Where V is the solution volume (L); M is the mass of monolithic adsorbents (g); and Co and Ce are the initial and equilibrium adsorbate concentrations, respectively. Other definition of adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions. Large surface area leads to high adsorption capacity and surface reactivity.

IV. EXPERIMENTAL MATERIALS AND METHOD

A. Adsorbent

The sawdust is carefully collected without any contamination from local area. After collection, sawdust is treated to make them ready for use. The sawdust is dried initially in an oven at about 80^{0}C and then ground to fine mesh and the particles size of 600-300 micron are separated by sieving through standard test sieves and then boiled in distilled water continuously for 30 minutes. The suspension was then left to settle to allow the supernatant to be poured off. This process is repeated several times until the coloured water-soluble components will removed completely. Finally the washed adsorbent was dried in an oven at 80 ^{0}C, allowed to cool and sieved into 600-300 micron for subsequent use.

B. Chemicals:

The test solution is prepared by diluting stock phenol solution (1000 mg/l) to the desired concentration. A stock solution is prepared by dissolving 0.1ml of phenol in distillate water and diluting it to 1000 ml. The prepared range of phenol concentration varies between (10 – 100) mg/l based on most common phenol concentrations range in industrial effluents which is (10-100) mg/l. The concentrations of residual phenol are measured using UV spectrophotometer equipment. The absorbance of the colored complex of phenol is read at characteristic wavelength of λ_{max}=270 nm.

C. Effects of Varying Parameters on Adsorption

pH

The pH value of the solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The pH of the solution would affect both aqueous chemistry and surface binding sites of the adsorbents. The effect of pH in turn depends on the charge on the adsorbent surface. If the adsorbent surface is negatively charged, at lower pH, the large number of H+ ions present neutralizes the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion, and a better adsorption is obtained. If the surface charge of the adsorbent is positively charged, the H+ ions may compete effectively with the cations of the solution causing a decrease in the amount of metal ion adsorbed.

Contact time

The amount adsorbed on to the adsorbent is in a state of dynamic equilibrium with the amount desorbed from the adsorbent. The time required to attain this state of equilibrium is termed as the equilibrium time. The amount adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under the operating conditions.

Temperature and Pressure

Increase of temperature and decrease of pressure increase the extent of adsorption. This fact that heat is absorbed in the process of adsorption is implied in the Le Chatliers principles. As in the case of the heat of the solution the different heats of adsorption, viz, the differential and integral heat must be distinguished. If accurate values were to be obtained the results would probably throw much light on the adsorption phenomena. Many attempts should be made to determine heats of adsorption experimentally.

Surface area (particle size)

The adsorbents with smaller particle size have a higher ability in the adsorption process with large external surface. Therefore more chemical ions can be removed than the large particles. The adsorption increases as the particle size decreases, because the surface area increases when the particle size decreases. Such an effect is probably due to the inability of the large ions to penetrate all the initial pore structure of the adsorbent.

Types of Adsorbents

Most of the adsorption researches have been concentrated on the use of bacteria and fungi for the removal of heavy metals. Both viable and inactive cells have been studied. This generally involves culturing of these microorganisms using chemicals. A potential economical alternative would be to use, naturally abundant materials such as waste biomass. These natural materials can be easily processed and used for metal removal, and hence can offer an economical solution to the problem of heavy metal pollution.

D Batch Adsorption

Batch adsorption experiment is conducted in order to determine the optimum adsorbent mass and equilibrium time, to generate adsorption kinetics data, adsorption isotherm data and the data used to derive response surface model equations. Blank solutions (solution without the adsorbent) are also included to check if there was any adsorption on the surface of the conical flask. Before the beginning of an adsorption experiment, the initial concentrations of all the adsorbates are determined. After equilibrium, the supernatant is separated by filtration. Final concentrations of the adsorbates are determined and the adsorption capacity, qe, was calculated as:

$$q_e = V\,(Co-Ce)/M$$

Where Co and Ce are the initial and equilibrium adsorbate concentrations in solution (mg/l), respectively, V is a known volume of synthetic wastewater (l), and m is a known mass of dry adsorbent (g).

$$\text{Percentage Removal} = (Co-Ce)/Co \times 100$$

E. Adsorption Isotherms

An adsorption isotherm represents a relationship between the amount of adsorbate that has been adsorbed at a constant temperature and its concentration in the equilibrium solution. It provides physiochemical data for assessing the applicability of the adsorption process as a complete unit operation. In our study, we assumed monolayer adsorption of phenol and applied the Langmuir and Freundlich isotherms to fit the equilibrium data of adsorption of phenol on sawdust.

Langmuir

The Langmuir isotherm is based on the assumption that adsorption takes place only at specific homogenous sites within the adsorbent surface with uniform distribution of energy level. Once the adsorbate attaches onto a site, no further adsorption can take place at that site and therefore the adsorption process is monolayer in nature. The linear form of the Langmuir equation is:

$$Ce/qe = 1/(Q_o b) + Ce/Q_o$$

Where Ce (mg/L) is the equilibrium concentration of phenol, qe (mg/g) is the amount of phenol adsorbed per unit mass of adsorbent, and Q_o (mg/g) and b (L/mg) are Langmuir constants related to adsorption capacity and rate of adsorption respectively. A graph of Ce/qe versus Ce would give a straight line having a slope of $1/Q_o$ and intercept of $1/Q_o b$.

Freundlich

The Freundlich model is an empirical equation based on adsorption onto a heterogeneous surface supporting sites of varied affinities. It is assumed that stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. The linear form of the Freundlich equation is:

$$\log (x/m) = \log kf + (1/n) \log Ce$$

Where x (mg) is the amount of phenol adsorbed and m (g) is the mass of adsorbent used, Ce (mg/L) is the equilibrium concentration of phenol in the solution, kf and n are Freundlich constants. A plot of log (x/m) versus log Ce gives a straight line having a slope 1/n and an intercept of log kf.

V. RESULT AND DISCUSSION

A Calibration of Solution

The solution of phenol is colorless. The equipment used for the measurement of phenol concentration is an Ultraviolet Visible Spectrometer. To establish a reference for measurements, a base line correction is carried out by filling both the cuvettes with the blank solution and using the option of base line correction on the spectrometer. The phenol solution is then placed into the sample cuvette to get a graph of the ultraviolet absorption of the solution over the range of characteristic wavelength λ_{max}=270 nm. A spectrophotometer is used for the calibration plot, which showed a linear variation up to 100 mg/l concentration. The value at the peaks which gives the wavelength of absorption for the given concentration of phenol is found out. The process is repeated for all concentrations of phenol and a graph of absorbance vs. concentration of phenol is plotted. The results are shown in Table IV and Fig.1.

TABLE IV
CALIBRATION OF PHENOL SOLUTION

Concentration of Phenol (mg/l)	Absorbance (%)
10	0.0002
20	0.515
30	0.7286
50	1.2086
70	1.7157
100	2.4689

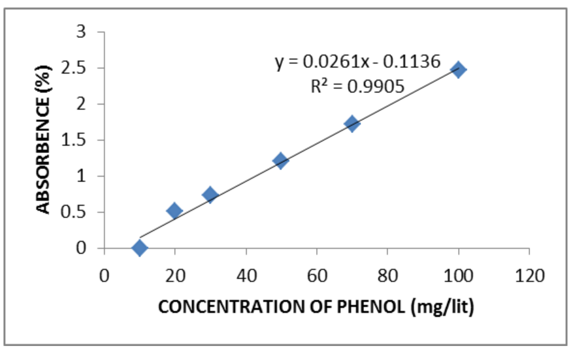

Fig. 1 Calibration graph for Phenol Concentration

B. FTIR for Sawdust

IR Spectra of Sawdust, the graphs taken between the wave numbers 4500 cm^{-1} and 500 cm^{-1} of sawdust. The peaks appearing in the FTIR spectrum were assigned to various functional groups according to their respective wave numbers. Group responsible for adsorption property at 3400-2400 cm^{-1} wave length shows very strong O-H bond. Again 1730-1700 cm^{-1} wave length shows C=O bond. Conjugation moves adsorption to a lower frequency. Again 1320-1210 cm^{-1} wave number shows C-O bond of medium intensity.

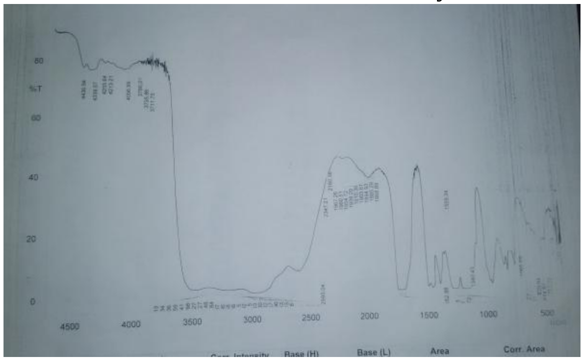

Fig. 2 FTIR spectra for Sawdust powder

VI. CONCLUSION

A review of adsorbent presented here shows a great potential for the elimination of toxic chemicals from Industrial wastewater. The sorption capacity is dependent on the type of the adsorbent investigated and the nature of the waste water treated. More studies should be carried out to better understand the process of low-cost adsorption and to demonstrate the technology effectively. This aspect need to be investigated further in order to promote large scale use of non-conventional adsorbents. If low cost adsorbents performance is well in removing heavy metals they can be adopted not only to minimize cost but also maximize the efficiency and profitability. The use of low cost absorbent may contribute to the sustainability of the surrounding. Phenols can bring major damage for aquatic organism and people, it is hard to eliminate it in a short time, and the writer summarizes some treatment methods of phenol in the industrial wastewater and suggests people to do further re-search in mechanism of degradation, biological culture development and degradation rate of phenol.

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