TREATABILITY STUDIES OF INDUSTRIAL WASTE WATER CONTAINING PHENOL USING COAGULATION-ADSORPTION TECHNIQUE

THESIS

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Declaration of originality and compliance of academic ethics

I hereby declare that this thesis contains literature survey and original research Work by the undersigned candidate, as part of his “***Master of Chemical Engineering*”** studies.

All information in this document have been obtained and presented in Accordance with academic rules and ethical conduct.

I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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CERTIFICATE OF RECOMMENDATION

This is to certify that Mr. Abhishek Anand, final year Master of Chemical Engineering (M.che) examination student of Department of Chemical Engineering, Jadavpur University (Examination Roll no. M4CHE1606; Regd. No. 128884 of 2014-2015), has completed the Project work titled "TREATIBILITY STUDIES OF INDUSTRIAL WASTE WATER CONTAINING PHENOL USING COAGULATION-ADSORPTION TECHNIQUE" under the guidance of Prof. Prasanta Kumar Banerjee and Prof. Siddhartha Datta during his Masters Curriculum. This work has not been reported earlier anywhere and can be approved for submission in partial fulfilment of the course work.

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DEDICATION

Special Dedication to my parents, friends and my

Respected project supervisor

For all your care, support and believe in me.

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ABSTRACT

Industrial phenolic waste water being corrosive, hazardous to environment and health issues is one of the major concerns associated with chemical and pharmaceutical industries such as petrochemical industries, petroleum refineries, coal gasification operations, pulp and paper mills and pharmaceutical industries etc. Methods like extraction, adsorption and ion exchange, advanced oxidation processes, photo-decomposition, electro-fenton method, coagulation, and adsorption have been applied for the treatment.

In this study combined effect of coagulation followed by adsorption have been used to increase the overall efficiency from 90% to about 97-99%.Coagulant Ferric Chloride($FeCl_3$) have shown better result in destabilization of colloidal particles, than other coagulants like Aluminium sulphate($Al_2(SO_4)_3$)**.** It has been confirmed by the result from characterization of treated water by measuring its TSS, TDS, PH, BOD & COD. Fly ash was used as an economical adsorbent which showed increased efficiency up to 98-99%. Factors like contact time, temperature, adsorbent dose, shaker speed & pH, have been studied to determine the optimal condition for adsorption. The optimum operating condition were (90 min, 150 rpm shaking speed, 45^{o}c, pH=4,100 mg adsorbent dose on 10 ppm phenol conc.). Isotherm, kinetics and thermodynamics study have been done to recognize the phenol adsorption on treated fly ash. The result showed that the adsorption process after coagulation with $Al_2(SO_4)_3$ followed 1st order kinetics & after coagulation with $FeCl_3$ followed 2nd order kinetics, pointing that the adsorption mechanism is physical adsorption process. Langmuir and Freundlich isotherm have been investigated. The thermodynamics parameters have been studied and it proved that adsorption of phenol is exothermic and spontaneous. This study convinced that the coagulation (with Ferric Chloride) followed by adsorption (with fly ash) proved to be an alternative, effective, economic, and environmental friendly process for phenol removal from industrial waste water.

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CHAPTER -1

INTRODUCTION

1. INTRODUCTION

In the past few decades, the rapid pace of industrialization, population expansion, and unplanned urbanization have contributed greatly to the severe pollution of water bodies and surrounding soils. The main sources of fresh water pollution can be attributed to discharge of untreated toxic industrial wastes and dumping of industrial effluents. Developing green and sustainable technology for the effluent treatment is very important research area in this era of industrial and social development. Many researchers have carried out the research in this field and found that phenol is one of the pollutants. It has its presence in the effluent from major chemical and pharmaceutical industries such as petrochemical industries, petroleum refineries, coal gasification operations, liquefaction process, resin manufacturing industries, dye synthesis units, pulp and paper mills and pharmaceutical industries. It is a highly corrosive and nerve poisoning agent. Phenol causes harmful side effects such as sour mouth, diarrhea, impaired vision, excretion of dark urine. Due to the toxic properties, including permeabilisation of cellular membranes and cytoplasm coagulation, phenolic contaminants can damage sensitive cells and cause profound health and environmental problems. The World Health Organization has limited phenol concentration in the water to 1 mg/L (WHO, 1994). It is also toxic for aquatic animals**.** Therefore, removal of phenol from industrial effluents is essential before discharging into water bodies.

Additionally, fairly intensive studies have inferred that these pollutants may undergo chemical and biological assimilations, eutrophication, consumes dissolved oxygen, prevent re-oxygenation in receiving streams and have a tendency to sequester metal ions accelerating genetoxicity and microtoxicity. In a wider sense, sporadic and excessive exposure to such effluents in water bodies is susceptible to a broad spectrum of immune suppression, respiratory, circulatory, central nervous and neuro behavioral disorders presage as allergy, auto immune diseases, multiple myeloma, leukemia, vomiting, hyperventilation, insomnia, profuse diarrhea, salivation, cyanosis, jaundice, quadriplegia, tissue necrosis, eye (or skin) infections, irritation to even lung edema. Today, nearly 70–80% of all illnesses in developing countries are related to water contamination.

The toxic levels usually range between the concentrations of 10-24 mg/L for human and the toxicity level for aquatic animal between 9-25 mg/L. Lethal blood concentration of phenol is around 150 mg/100 ml. Various treatment processes used for the removal and/or recovery of phenols are hot gas or steam stripping, adsorption, ion exchange solvent extraction, oxidation, phase transfer catalysis and biological treatment processes. In this study phenolic waste water is treated using coagulation followed by adsorption process.

1.1 NATURE & CHARACTERISTICS OF INDUSTRIAL WASTE WATER

It is only natural for industry to presume that its wastewater can best be disposed of in the domestic sewer system. However, city authorities should not accept any waste water discharges into the domestic sewer system without first learning the facts about the characteristics of the waste water, the sewage system’s ability to handle them, and the effects of the waste water upon all components of the city disposal system. Institution of a sewer ordinance, restricting the types or concentrations of waste water admitted in the sewer leading to a treatment plant, is one means of protecting the system. Secondary treatment standards for waste water are concerned with the removal of biodegradable organics, suspended solids, and pathogens. Many of the more stringent standards that have been developed recently deal with the removal of nutrients and priority pollutants. When waste water is to be re used, standards normally include requirements for the removal of refractory organics, heavy metals, and in some cases dissolved inorganic salts.

1.1.1 Physical Characteristics:

The most important physical characteristic of waste water is its total solids content, which is composed of floating matter, settleable matter, colloidal matter, and matter in solution. Other important physical characteristics include odour, temperature, colour, and turbidity.

a) Total Solids

Analytically the total solids content of a waste water is defined as all the matter that remains as residue upon evaporation at 103 to 105 °C. Matter that has a significant vapour pressure at this temperature is lost during evaporation & is not defined as a solid. Settleable solids are those solids that will settle to the bottom of a cone shaped container (called an Imhoff cone) in a 60 minute period.

Settleable solids, expressed as mg/L, are an approximate measure of the quantity of sludge that will be removed by primary sedimentation. Total solids, or residue upon evaporation, can be further classified as non-filterable (suspended) or filterable by passing a known volume of liquid through a filter. The filterable solids fraction consists of colloidal and dissolved solids. The colloidal fraction consists of the particulate matter with an approximate size range of from 0.001 to 1 µm. The dissolved solids consist of both organic & inorganic molecules and ions that are present in true solution in water. The colloidal fraction cannot be removed by settling. Generally, biological oxidation or coagulation, followed by sedimentation, is required to remove these particles from suspension. The suspended solids are found in considerable quantity in many industrial waste water, such as cannery and paper mill effluents. They are screened and/or settled out at the treatment plant. Solids removed by settling and separated from wash water are called sludge, which may then be pumped to drying beds or filtered for extraction of additional water (dewatering).

Each of the categories of solids may be further classified on the basis of their volatility at 550 $\pm$ 50^{o}C. The organic fraction will oxidize and will be driven off as gas at this temperature, and the inorganic fraction remains behind as ash. Thus the terms "Volatile suspended solids" and "Fixed suspended solids" refer, respectively, to the organic and inorganic (or mineral) content of the suspended solids. The volatile solids analysis is applied most commonly to waste water sludge to measure their biological stability.

b) Odour

Odour is usually caused by gases produced by the decomposition of organic matter or by substances added to the waste water. Industrial waste water may contain either odours compounds or compounds that produce odour during the process of waste water treatment.

c) Temperature

The temperature of water is a very important parameter because of its effect on chemical reactions and reaction rates, aquatic life, and the suitability of the water for beneficial uses. Increased temperature, for example, can cause a change in the species of fish that can exist in the receiving water body. Industrial establishments that use surface water for cooling water purposes are particularly concerned with the temperature of the intake water.

In addition, oxygen is less soluble in warm water than in cold water. The increase in the rate of biochemical reactions that accompanies an increase in temperature, combined with the decrease in the quantity of oxygen present in surface waters, can often cause serious depletions in dissolved oxygen concentration in the summer months. When significantly large quantities of heated water are discharged to natural receiving water, these effects are magnified. It should also be realized that a sudden change in temperature can result in a high rate of mortality of aquatic life. Moreover, abnormally high temperatures can foster the growth of undesirable water plants and waste water fungus.

d) Colour

Colour of industrial waste water varies according to the type of industry. Knowledge of the character and measurement of colour is essential. Since most coloured matter is in a dissolved state, it is not altered by conventional primary devices, although secondary treatment units, such as activated sludge and trickling filters, remove a certain percentage of some types of coloured matter. Sometimes colour matters needs chemical oxidation procedures for removal.

e) Turbidity

Turbidity, a measure of the light transmitting properties of water, is another test used to indicate the quality of waste water discharges and natural water with respect to colloidal and residual suspended matter. In general, there is no relationship between turbidity and the concentration of suspended solids in untreated waste water. There is, however, a reasonable relationship between turbidity and suspended solids for the settled secondary effluent from the activated sludge process.

1.1.2 Chemical Characteristics

a) Organic Matter

Organic compounds are normally composed of a combination of carbon, hydrogen, and oxygen, together with nitrogen in some cases. Other important elements, such as sulfur, phosphorus, and iron, may also be present. Also, industrial waste water may contain small quantities of a large number of different synthetic organic molecules ranging from simple to extremely complex in structure. Typical examples include surfactants, organic priority pollutants, volatile organic compounds and agricultural pesticides. The presence of these substances has complicated industrial waste water treatment because many of them either cannot be or are very slowly decomposed biologically.

Fats, Oils, and Grease. Fats are among the more stable of organic compounds and are not easily decomposed by bacteria. Kerosene, lubricating oils reach the sewer from workshops and garages, for the most part they float on the waste water, although a portion is carried into the sludge on settling solids. To an even greater extent than fats, oils, and soaps, the mineral oils tend to coat surfaces causing maintenance problems. If grease is not removed before discharge of the waste water, it can interfere with the biological life in the surface waters and create unsightly floating matter and films. The oil and grease (O & G) is a very important test used to determine the hydrocarbon content of industrial waste waters. O&G tests include free O&G and emulsified O&G measures. These tests will determine the type of treatment required. Free O&G can be removed by flotation & skimming using gravity oil separator (GOS). However, emulsified oil is removed by Dissolved Air Flotation system after chemical de-emulsification of oil. In any case, O&G have to be removed prior biological treatment as they will clog the flow distributing devices and air nozzles.

Surfactants. Surfactants are large organic molecules that are slightly soluble in water and cause foaming in waste water treatment plants and in surface waters into which the waste water effluent is discharged. Surfactants tend to collect at the air water interface. During aeration of waste water, these compounds collect on the surface of the air bubbles and thus create a very stable foam.

Volatile Organic Compounds (VOCs). Organic compounds that have a boiling point less than 100^oC and/or a vapour pressure greater 1 mm Hg at 25^oC are generally considered to be volatile organic compounds (VOCs). The release of these compounds in sewers and at treatment plants is of particular concern with respect to the health of collection system and treatment plant workers.

Pesticides & Agricultural Chemicals. Trace organic compounds, such as pesticides, herbicides, and other agricultural chemicals, are toxic to most life forms and therefore can be significant contaminants of surface waters.

b) Inorganic Matter

Several inorganic components of waste water are important in establishing and controlling waste water quality. Industrial waste water has to be treated for removal of the inorganic constituents that are added in the use cycle. Concentrations of inorganic constituents also are increased by the natural evaporation process, which removes some of surface water and leaves the inorganic substance in the waste water.

pH. The hydrogen ion concentration is an important quality parameter of waste water. The concentration range suitable for the existence of most biological life is quite narrow and critical. Waste water with an adverse concentration of hydrogen ion is difficult to treat by biological means, and if the concentration is not altered before discharge, the waste water effluent may alter the concentration in the natural waters.

Alkalinity. Alkalinity in waste water results from the presence of the hydroxides, carbonates, and bicarbonates of elements such as calcium, magnesium, sodium, potassium, or ammonia. Of these, calcium and magnesium bicarbonates are most common. Borates, silicates, phosphates, and similar compounds can also contribute to the alkalinity. The alkalinity in waste water helps to resist changes in pH caused by the addition of acids. The concentration of alkalinity in waste water is important where chemical treatment is to be used, in biological nutrient removal, and where ammonia is to be removed by air stripping.

Nitrogen. Because nitrogen is an essential building block in the synthesis of protein, nitrogen data will be required to evaluate the treatability of waste water by biological processes. Insufficient nitrogen can necessitate the addition of nitrogen to make the waste water treatable. Where control of algal growth in the receiving water is necessary to protect beneficial uses, removal or reduction of nitrogen in waste waters prior to discharge may be desirable. The total nitrogen, as a commonly used parameter, consists of many numerous compounds such as; NH_3, NH_4-N, NO_3-N, NO_2-N, urea, organic-N (amines, amino acids, ...etc).

Phosphorus. Phosphorus is also essential to the growth of algae and other biological organisms due to its presence in DNA. The organically bound phosphorus is an important constituent of industrial waste water and sludge.

Sulfur. Sulfate is reduced biologically under anaerobic conditions to sulfide, which in turn can combine with hydrogen to form hydrogen sulfide (H_2S). Hydrogen sulfide released to the atmosphere above the waste water in sewers that are not flowing full tends to accumulate at the crown of the pipe. The accumulated H_2S can then be oxidized biologically to sulfuric acid, which is corrosive to steel pipes and equipment.

Toxic Inorganic Compounds.

Because of their toxicity, certain cations are of great importance in the treatment and disposal of waste water. Many of these compounds are classified as priority pollutants. Copper, lead, silver, chromium, arsenic, and boron are toxic in varying degrees to microorganisms and therefore must be taken into consideration in the design of a biological treatment plant. Many plants have been upset by the introduction of these ions to the extent that the microorganisms were killed and treatment ceased. Other toxic cations include potassium and ammonium at 4000 mg/L. Some toxic anions, including cyanides and chromates, are also present in industrial waste water. These are found particularly in metal plating waste water and should be removed by pre-treatment at the site of the industry rather than be mixed with the municipal waste water. Fluoride, another toxic anion, is found commonly in waste water from electronics manufacturing facilities. Organic compounds present in some industrial waste water are also toxic.

Heavy Metals.

Trace quantities of many metals, such as nickel (Ni), manganese (Mn), lead (Pb), chromium (Cr), cadmium (Cd), zinc (Zn), copper (Cu), iron (Fe), and mercury (Hg) are important constituents of some industrial waste waters. The presence of any of these metals in excessive quantities will interfere with many beneficial uses of the water because of their toxicity; therefore, it is frequently desirable to measure and control the concentration of these substances.

1.1.3 Biological Characteristics

Some industries have certain pathogenic organisms like slaughter houses, others have molds and fungi like starch and yeast factories. Biological tests on waste water determine whether pathogenic organisms are present by testing for certain indicator organisms. Biological information is needed to assess the degree of treatment of the waste water before its discharge to the environment. The parameters setting the standards for the discharge of different industrial waste water effluents are outlined in table. Total nitrogen is a commonly used parameter that includes a number of parameters, NH_3, NH_4-N, NO_3-N, NO_2-N, urea, organic nitrogen such as amines, amino acids, proteins, etc.) and process chemicals. The presence of these compounds depends on the production.

1.2 INDUSTRIAL POLLUTANTS:

Industrial waste waters contain pollutants that can be divided into two types (conventional or toxic) depending on their degree of impact on the environment.

CONVENTIONAL POLLUTANTS. Conventional pollutants are BOD, TSS, pH, fecal coliform, oil, and grease.

TOXIC POLLUTANTS. Sixty five specific compounds and families of compounds were identified as toxic by the EPA. The EPA must promulgate effluent limitations, pretreatment standards, and new source performance standards for 42 major industrial categories. Examples of toxic substances typically found in waste water are heavy metals, cyanides, aqueous film forming foam, phenols and halogenated phenols, paint stripping agents, solvents, surfactants, and degreasers.

a) Contact local and state regulatory agencies for an updated list of priority pollutants.

b) If characteristics of industrial waste water are unknown, obtain complete organic and inorganic analysis by an EPA certified laboratory.

1.2.1) Sources of phenols and phenolic Compounds

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, phenol formaldehyde plants, bisphenol–A and other synthetic resin manufacturing units. Table-1 presents some of the industrial waste water comparatively rich with phenol along with their phenol concentration.

Table 1: Concentration of phenolic compounds in industrial waste water

Sl. No.	**Sources of waste water**	**Phenol Concentration mg/L**
1.	Coal Carbonisation process	
	a) Low temperature	1000-1800
	b) High temperature	800-1000
2.	Metallurgical coke manufacturing process	
	a) Spent liquor after phenol recovery	900-1000
	b) Coke oven effluent	35-250
3.	Oil Refineries	1500-2000
4.	Phenol formaldehyde resin manufacturing plants	800-2000

1.3 VARIOUS METHODS FOR PHENOL REMOVAL:

a) Electro coagulation

Abdelwahab et.al. have carried out the research on electrochemical removal of phenol from oil refinery waste. They explored the possibility of using electro coagulation for phenol removal. They used the cell with horizontally oriented aluminum cathode and a horizontal Aluminium screen anode. They studied the phenol removal with respect to various parameters such as pH, operating time, current density, initial phenol concentration and addition of NaCl. According to them removal of phenol during electro coagulation was due to combined effect of sweep coagulation and adsorption. The results showed that, at high current density and solution pH of 7, remarkable removal of 97% of phenol after 2 hour can be achieved. Also they observed that the rate of electro coagulation increases with decrease in phenol concentration and the maximum removal rate was attained at 30 mg/L phenol concentration. The study showed that, electro coagulation of phenol using aluminum electrodes is a promising process. Effect of the variables like pH, operating time, current density, initial phenol concentration and addition of NaCl on phenol removal by coagulation was studied by Zazouli and Taghavi. They observed maximum phenol removal percentage at a pH value of 7. They also observed that increasing the concentration of phenol led to decrease in the removal efficiency. They also observed that the removal rate of phenol increased with increasing current density, and the highest current density (25 mA/cm^2) had the maximum removal efficiency. Ashtoukhy et. al. have carried out the research on treatment of petrochemical waste water containing phenolic compounds by electro coagulation using a fixed bed electrochemical reactor. They explored the possibility of using electro coagulation to remove phenolic compounds from oil refinery waste effluent using an electrochemical reactor with a fixed bed anode made of randomly oriented Aluminium rasching rings packed in a perforated plastic basket located above the horizontal cathode.

b) Extraction

The extraction of phenol from simulated sebacic acid waste water was tried by Rao et. al. They used 1-hexanol, 1-heptanol and 1-octanol as solvent for phenol removal. It was observed that 1-octanol showed lesser phenol removal efficiency compared to other two solvents. Xu et. al. have carried out investigation on extraction of phenol in waste water with annular centrifugal contactors. They carried out the experimental study on treating the waste water containing phenol with QH-1extractant (the amine mixture) and annular centrifugal contactors. They observed that the extraction rate of the three stage cascade was more than 99%. When 15% NaOH was used for stripping of phenol in QH-1(the amine mixture), the stripping efficiency of the three stage cascade was also more than 99% under the experimental conditions.

c) Photodecomposition

Investigation of the photodecomposition of phenol in near UV-irradiated aqueous TiO_2 suspensions was carried out by Ilisz et. al. They investigated the effects of charge trapping species on the kinetics of phenol decomposition. They observed that the heterogeneous degradation of phenol followed apparently zero order kinetics up to 70% conversion. The results of the experiments in the presence of Ag^+ indicated that the photo transformation of phenol can proceed via direct electron transfer, neither dissolved O_2 nor its reduced forms play a significant role in the degradation mechanism. Akbal and Onar have studied photo catalytic degradation of phenol. They carried out the investigation to study photo catalytic degradation of phenol in the presence of UV irradiated TiO_2 catalyst and H_2O_2. They concluded that photo catalytic degradation can be effective method for phenol removal.

d) Biological Methods

Marrot et.al have carried out the research on biodegradation of high phenol concentration by activated sludge in an immersed membrane bioreactor. They investigated the effect of adaption of mixed culture on phenol degradation. They found that biological treatment was economical and practical for removal of phenol. High concentrations of phenol are inhibitory for growth. Biological and enzymetric treatments were used for phenol removal by Bevilaqua et. al. The systems studied were conventional batch aerobic biological followed or preceded by enzymatic treatment. They employed the Tyrosinase as enzyme. They observed that biological treatment effectively degrades phenol up to concentration of 420 mg/L. Enzymatic polishing of bio treated effluent removed up to 75% of the remaining phenol in a four hour reaction with 46 ml of tyrosinase and 50 mg/L of chitosan (used as coagulant). The research on detection of phenol degrading bacteria and pseudomonas putida in activated sludge by polymerase chain reaction was carried out by Movahedyan. According to results in this study, the best phenol degrading bacteria that can utilize 500–600 mg/L phenol completely after 48 hours incubation belong to Pseudomonas Putida strains. It is clear that use of isolated bacteria can lead to considerable decrease of treatment time as well as promotion of phenol removal rate. Tziotzios et. al. have reported research on biological phenol removal. They carried out research to study the efficiency of packed bed reactor on phenol biodegradation and effect of specific area of specific material on biodegradation efficiency. They used the indogeneous bacteria from olive pulp. The maximum phenol removal rate was observed to be 12.65 gram per litre per day, when filled with gravel support material under draw fill operation. Same operation with plastic packing showed maximum phenol removal of 4.3 grams per litre per day. A review on recent advances in biodegradation of phenol was carried out by Basha et al.Comparative study of free and immobilized growth was carried out by Pishgar et. al. They observed that the culture was able to degrade the phenol up to 700 mg/L. The immobilized cells were able to remove phenol at concentration of 100 to 700 mg/L in a slightly shorter time period. The biodegradation rate of phenol improved when immobilized cells were applied. Kinetic Studies for an aerobic packed bed biofilm reactor for treatment of organic waste water with and without phenol was carried out by Dey and Mukharjee. They carried out studies on removal efficiency of COD and phenol in a mixture of carbohydrate and phenol. The aerobic bioreactor with the glass beads was used for the purpose. They concluded that the performance of the bioreactor decreased marginally under 50 mg/L phenol charging along with other carbohydrate in the influent waste water. At this condition, phenol removal rate of 89% was achieved. Almsi et. al. have carried out the work related to anaerobic waste water stabilization pond for phenol removal. The phenol removal efficiency was found to 90 percent. According to the study, anaerobic ponds with petroleum waste water is attractive alternative than many other methods. Removal of phenol by using rotating biological contactors was tried by Pradip et.al. They examined the impact of process variables, viz concentration, rotational speed and percentage submergence of the disc on phenol removal.

e) Electro-Fenton (EF-Fere) method

An improved Electro-Fenton (EF-Fere) method using H_2O_2 amendments and electro generated ferrous ions was investigated to treat phenol containing waste water by Jiang et.al.. The degradation process of phenol was carried out in an EF-Fere system, which was composed of a power source, a cylindrical electrolytic cell and a H_2O_2 dosing system. The electrolysis was controlled by an electrochemical working station. For the phenol degradation experiments conducted in the EF-Fere electrolytic system, the maximum COD removal efficiency of phenol containing waste water is achieved at the condition of 800 mg/L initial ferric ions concentration, 1.0A electric current with continuous H_2O_2 addition mode.

f) Advanced oxidation processes

Rubalcaba et. al. have used advanced oxidation processes coupled to a biological treatment for phenol remediation. Results showed promising research ways for the development of efficient coupled processes for the treatment of waste water containing toxic or non-biodegradable compounds. Similar research has been carried out by Esplugas et. al.. Though Fenton reagent was most effective for degradation of phenol. Lower costs were obtained with ozonation. In the ozone combinations, the best results were achieved with single ozonation. Phenol degradation in presence of chlorides and sulphates was carried out by Siedlecka et. al. They studied the degradation of three representatives of phenolic compounds in presence of chlorides and sulphates, namely phenol, 2-chlorophenol and 2-nitrophenol. The presence of anions influenced the degradation rates. Relatively low degradation rates were observed for 2- chlorophenol. The biodegradability of phenol was increased by chloride while that of other two derivatives was increased by presence of sulphates.

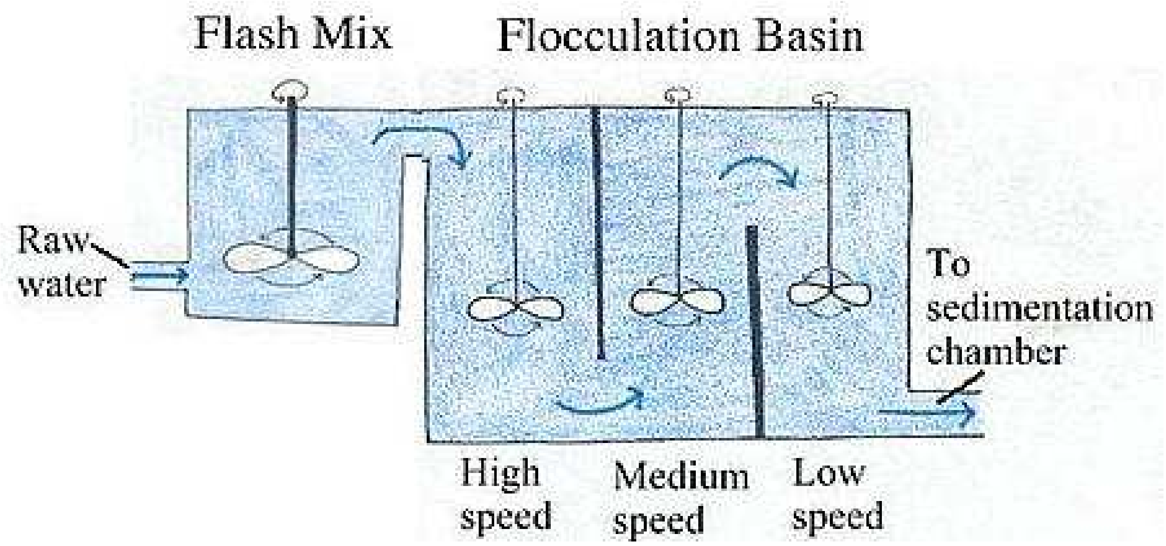
g) Adsorption and Ion exchange

Experiments were conducted to examine the liquid phase adsorption of phenol from water by silica gel, activated alumina, activated carbon by Roostaei and Tezel. Experiments were carried out for the analysis of adsorption equilibrium capacities and kinetics. They found it to be a promising method for phenol removal. The research on phenol removal from aqueous solution by adsorption and ion exchange mechanisms onto polymeric resins was done by Caetano et.al. They evaluated the removal of phenol from aqueous solution by using a non functionalized hyper cross linked polymer macro net and two ion exchange resins. The non functionalized resin reported the maximum loading adsorption under acidic conditions, where the molecular phenol form predominates. Ion exchange resins showed the maximum removal in alkaline medium. Desorption of non functionalized resin was achieved by using the solution (50% v/v) of methanol/water with a recovery close to 90%. In the case of the ion exchange resins the desorption process was performed at different pHs. Qadir and Rhan have investigated the removal of phenol by using adsorption. The treatment of waste with active carbon is considered to be an effective method for the removal of phenol from waste solution because of its large surface area. The experimentation on adsorption isotherms for phenol removal on activated carbon was carried out by Maarof et.al. The adsorption isotherm parameters for the Langmuir and Freundlich models were determined using the adsorption data. It was found that both the Langmuir and the Freundlich isotherms described well the adsorption behavior of phenol on Norit Granular Activated Carbon) NAC 010, while the Freundlich isotherm described very well the adsorption of phenol on NAC 1240. Jadhav and Vanjara have carried out the research on adsorption of phenol sawdust, polymerized saw dust and sawdust carbon. They studied the influence of the parameters like concentration, agitation speed, amount of adsorbent and the pH on adsorption capacity. Hycinthe as adsorbent was used for phenol removal by Uddin et.al. They carried out the batch kinetic and isotherm studies under varying experimental conditions of contact time, phenol concentration, adsorbent dosage and pH. The infered that the adsorption of phenol decreased with increasing pH. The results also showed that kinetic data followed closely to the pseudo-second-order model. Activated carbons prepared from date stones was used for removal of phenolic compounds from aqueous solutions by adsorption by Dhidan. He used activated carbon prepared from date stones by chemical activation with ferric chloride as an adsorbent to remove phenolic compounds such as phenol and p-nitro phenol from aqueous solutions. He achieved the maximum phenol removal of 98% at pH value of 5 and 90 minutes of contact time. Kadhim and Al-Seroury have carried out research on characterization the removal of phenol from aqueous solution in fluidized bed column by rice husk adsorbent. They found that the pretreatment of rice husk increase the specific surface area and changed the functional groups , therefore leads to increase in the capacity of adsorption. Kulkarni et. al. have investigated the phenol removal from the effluent by using activated carbon in batch and fluidized bed experimentation. In batch studies they studied the effects of various parameters like adsorbent dose, pH, particle size on rate of adsorption. In case of fluidized bed, the effect of various parameters like concentration, fluid flow rate and adsorbent particle size were studied. The percentage decrease in phenol concentration increases with increase in adsorbent dose. With a reduction in particle size, initially steep increase in percentage removal of phenol is observed and it becomes more significant for finer particles. In case of fluidized beds, Increase in fluid flow rate gives better adsorption in case of activated carbon. In the present study particle size of 0.420 mm is found more beneficial. Girish and Murti have studied the potential of various low cost adsorbents for phenol removal. This review indicated that these agricultural materials have equivalent or even more adsorption capacity to activated carbon. Lua and Jia have used oil palm shell activated carbon in a fixed bed adsorber for phenol removal. The used the adsorption using the activated carbon derived from oil palm shells for the phenol, which they found to be very effective.

A research on mass transfer coefficients in a packed bed using tamarind nut shell activated carbon to remove phenol was done by Goud et. al. They reported work on the preparation and characterization of activated carbon from tamarind nutshell, an agricultural waste by product, and its use in a packed bed for the removal of phenol. They found that that the sorption of phenol is dependent on both the flow rate and the particle size of the adsorbent, and that the break point time and phenol removal yield decrease with increasing flow rate and particle size. For mass transfer coefficient, experimental values were in excellent agreement with the predicted values from the correlation. The experimentation for examining the application of adsorption packed bed reactor model for phenol removal was done by Sorour et.al. They conducted the experiments to determine the Langmuir equilibrium coefficients and to determine the bulk sorbate solution concentration for different adsorption column depths and different time as well. They predicted a packed bed model which was in well agreement with the laboratory data. They reported the sorption capacity per unit bed volume and rate constant to be 578.4 mg/L and 1.18 L/mg/min, respectively. Kulkarni et.al. have used tamarind bean activated carbon for phenol removal in fluidized bed. They studied the effect of various parameters like concentration, fluid flow rate and adsorbent particle size. They observed that it is observed that as the concentration increases the percent saturation of adsorbent increases. Also increase in fluid flow rate gives better adsorption.

1.4 Coagulation

After the source water has been screened and has passed through the optional steps of pre-chlorination and aeration, it is ready for coagulation and flocculation.



In theory and at the chemical level, coagulation and flocculation is a three step process, consisting of flash mixing, coagulation, and flocculation. However, in practice in the treatment plant, there are only two steps in the coagulation/flocculation process - the water first flows into the flash mix chamber, and then enters the flocculation basin.

Purpose

The primary purpose of the coagulation/flocculation process is the removal of turbidity from the water. Turbidity is a cloudy appearance of water caused by small particles suspended therein. Water with little or no turbidity will be clear.

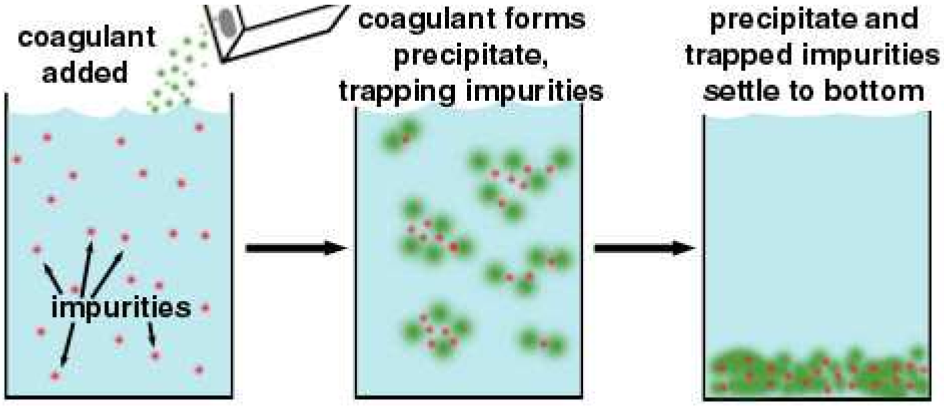
Turbidity is not only an aesthetic problem in water. Water with a high turbidity can be very difficult or impossible to properly disinfect. As a result, the maximum allowable level of turbidity in water is 0.5 NTU, while the recommended level is about 0.1 NTU. (NTU, or TU, stands for nephelometric turbidity units, a measurement of the turbidity of water.)

In addition to removing turbidity from the water, coagulation and flocculation is beneficial in other ways. The process removes many bacteria which are suspended in the water and can be used to remove colour from the water.

Turbidity and colour are much more common in surface water than in ground water. As surface water flows over the ground to streams, through streams, and then through rivers, the water picks up a large quantity of particles. As a result, while aeration is more commonly required for ground water, treatment involving coagulation and flocculation is typical of surface water.

Three Steps

As I mentioned above, the chemistry of coagulation/flocculation consists of three processes - flash mix, coagulation, and flocculation. Each of these processes is briefly explained below.



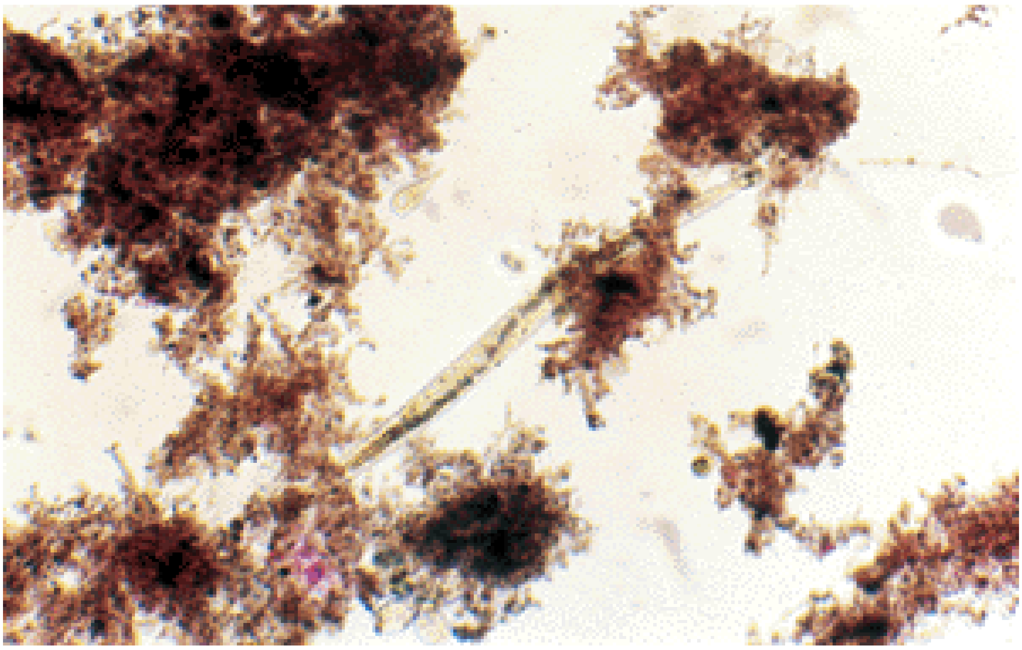
In the flash mixer, coagulant chemicals are added to the water and the water is mixed quickly and violently. The purpose of this step is to evenly distribute the chemicals through the water. Flash mixing typically lasts a minute or less. If the water is mixed for less than thirty seconds, then the chemicals will not be properly mixed into the water. However, if the water is mixed for more than sixty seconds, then the mixer blades will shear the newly forming floc back into small particles.

After flash mixing, coagulation occurs. During coagulation, the coagulant chemicals neutralize the electrical charges of the fine particles in the water, allowing the particles to come closer together and form large clumps. You may already be familiar with the process of coagulation from cooking. You can see coagulation occurring when preparing gelatin or when cooking an egg white.

The final step is flocculation. During flocculation, a process of gentle mixing brings the fine particles formed by coagulation into contact with each other. Flocculation typically lasts for about thirty to forty-five minutes. The flocculation basin often has a number of compartments with decreasing mixing speeds as the water advances through the basin. This compartmentalized chamber allows increasingly large floc to form without being broken apart by the mixing blades.

Floc

The end product of a well-regulated coagulation/flocculation process is water in which the majority of the turbidity has been collected into floc, clumps of bacteria and particulate impurities that have come together and formed a cluster. The floc will then settle out in the sedimentation basin, with remaining floc being removed in the filter.



The best floc size is 0.1 to 3 mm. Larger floc does not settle as well and is more subject to breakup in the flocculation basin. Smaller floc also may not settle.

1.4.1. Types of Coagulants

Coagulant chemicals come in two main types - primary coagulants and coagulant aids. Primary coagulants neutralize the electrical charges of particles in the water which causes the particles to clump together. Coagulant aids add density to slow settling flocs and add toughness to the flocs so that they will not break up during the mixing and settling processes.

Primary coagulants are always used in the coagulation/flocculation process. Coagulant aids, in contrast, are not always required and are generally used to reduce flocculation time.

Chemically, coagulant chemicals are either metallic salts (such as alum) or polymers. Polymers are man-made organic compounds made up of a long chain of smaller molecules. Polymers can be either cationic (positively charged), anionic (negatively charged), or nonionic (neutrally charged.) Different sources of water need different coagulants, but the most commonly used are alum and ferric sulfate.

$$Al_2(SO_4)_3 + 3\,Ca(OH)_2 \longrightarrow 2\,Al(OH)_3 + 3CaSO_4$$

Alum Lime

$$Fe_2(SO4)_3 + 3\,Ca(OH)_2 \longrightarrow 2\,Fe(OH)_3 + 3CaSO_4$$

Ferric Sulphate Floc

1.4.2 Factors Influencing Coagulation

In a well run water treatment plant, adjustments are often necessary in order to maximize the coagulation/flocculation process. These adjustments are a reaction to changes in the raw water entering the plant. Coagulation will be affected by changes in the water's pH, alkalinity, temperature, time, velocity and zeta potential.

The effectiveness of a coagulant is generally pH dependent. Water with a colour will coagulate better at low pH (4.4-6) with alum.

Alkalinity is needed to provide anions, such as (OH) for forming insoluble compounds to precipitate them out. It could be naturally present in the water or needed to be added as hydroxides, carbonates, or bicarbonates. Generally 1 part alum uses 0.5 parts alkalinity for proper coagulation.

The higher the temperature, the faster the reaction, and the more effective is the coagulation. Winter temperature will slow down the reaction rate, which can be helped by an extended detention time. Mostly, it is naturally provided due to lower water demand in winter.

Time is an important factor as well. Proper mixing and detention times are very important to coagulation.

The higher velocity causes the shearing or breaking of floc particles, and lower velocity will let them settle in the flocculation basins. Velocity around 1 ft/sec in the flocculation basins should be maintained.

Zeta potential is the charge at the boundary of the colloidal turbidity particle and the surrounding water. The higher the charge the more is the repulsion between the turbidity particles, less the coagulation, and vice versa. Higher zeta potential requires the higher coagulant dose. An effective coagulation is aimed at reducing zeta potential charge to almost zero.

1.5 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.

In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physicsorption (characteristic of weak Van Der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction.

As the adsorption progress, an equilibrium of adsorption of the solute between the solution and adsorbent is attained (where the adsorption of solute is from the bulk onto the adsorbent is minimum). The adsorption capacity (qe, m mol g^{-1}) of the molecules at the equilibrium step was determined according to the following equation:

$$q_e = V(C_o - C_e)/M$$

where V is the volume of solution (L); M is the mass of monolithic adsorbents (g); and C_o and C_e 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 .

1.5.1 Types of adsorbents

Different types of adsorbents are classified into natural adsorbents and synthetic adsorbents. Natural adsorbents include charcoal, clays, clay minerals, zeolites, and ores. These natural materials, in many instances are relatively cheap, abundant in supply and have significant potential for modification and ultimately enhancement of their adsorption capabilities. Synthetic adsorbents are adsorbents prepared from Agricultural products and wastes, house hold wastes, Industrial wastes, sewage sludge and polymeric adsorbents. Each adsorbent has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces. Many waste materials used include fruit wastes, coconut shell, scrap tyres, bark and other tannin rich materials, sawdust, rice husk, petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, clays, red mud, zeolites, sediment and soil, ore minerals etc.

Activated carbons as adsorbent for organic pollutants consists in their adsorption a complex process and there still exists considerable difficulty. The main cause of this difficulty results from the large number of variables involved. These include, for example, electrostatic, dispersive and chemical interactions, intrinsic properties of the solute (for example solubility and ionization constant), intrinsic properties of the adsorbent (such pore size distribution), solution properties (in particular, pH) and the temperature of the system.

Activated carbons (AC) (both granular activated carbon (GAC) and powdered activated carbons (PAC)) are common adsorbents used for the removal of undesirable odour, colour, taste, and other organic and inorganic impurities from domestic and industrial waste water owing to their large surface area, micro porous structure non-polar character and due to its economic viability. The major constituent of activated carbon is the carbon that accounts up to 95% of the mass weight In addition, active carbons contain other hetero atoms such as hydrogen, nitrogen, sulfur, and oxygen. These are derived from the source raw material or become associated with the carbon during activation and other preparation procedures. Putra et al. investigated the removal of Amoxicillin (antibiotic) from pharmaceutical effluents using bentonite and activated carbon as adsorbents. The study was carried out at several pH values. Langmuir and Freundlich models were then employed to correlate the equilibrium data on which both models fitted the data equally well. While chemisorption is the dominant adsorption mechanism on the bentonite, both physicosorption and chemisorption played an important role for adsorption onto activated carbon.

Adsorption of methane on granular activated carbon (GAC) was studied. The results showed that with decreasing temperature or increasing methane uptake by GAC the adsorption efficacy decreased. Interactions between the methane molecules and the surface of carbon increase the density of adsorbed methane in respect to the density of compressed gas. The effect that the porosity and the surface chemistry of the activated carbons have on the adsorption of two VOC (benzene and toluene) at low concentration (200 ppm) was also studied. The results show that the volume of narrow micro pores (size <0.7 nm) seems to govern the adsorption of VOC at low concentration, specially for benzene adsorption. AC with low content in oxygen surface groups has the best adsorption capacities.

Chapter -2

AIM AND OBJECTIVE OF WORK

2.1 AIM

- ✓ Treatment of phenolic waste water by Coagulation-Adsorption process.

2.2 OBJECTIVE

- ✓ Efficient, low cost methods of phenol removal from aqueous solutions using different coagulants and low cost adsorbent.
- ✓ Study of different parameters that affect the adsorption process like pH, agitation speed, adsorbent dose, initial Phenol concentration, contact time & temperature etc.
- ✓ Study of different parameters that affect the coagulation process like pH, TSS, TDS, BOD & COD.
- ✓ To determine the effective coagulant & adsorbent doses.
- ✓ Study of Isotherm, kinetics and thermodynamics, mass transfer of the adsorption process.
- ✓ Comparative study of the effectiveness of chemical coagulants with adsorbents.

Chapter-3

BACKGROUND OF THE WORK

BACKGROUND OF THE WORK

This chapter provides some information about the literature surveyed and reviewed to perform the present investigation. Various coagulants and adsorbents were used for the treatment of industrial waste water all over the world for the last few years. Here an attempt has been made to identify some coagulant and low cost adsorbent for coagulation-adsorption process by studying some journals. Summary of some research papers are listed below...

1) Lesley Joseph , Joseph R.V. Flora , Yong Gyun Park , Mohammed Badawy ,and Hazem Saleh , worked on the topic "Removal of natural organic matter by combined effect of coagulation & adsorption" by using carbon nanomaterials which showed single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) was used for the removal of natural organic matter(NOM) from various water sources. PAC was used for comparison. The adsorption capacity of SWCNTs was greater than that of MWCNTs for the source waters.PAC often outperformed MWCNTs in these combined treatment processes, except in the case of the young leachate. The results of this study show that combined coagulation–adsorption treatment using carbon nanomaterials can be effective in removing NOM from various water sources. This work had been published in journal "Separation and Purification Technology 95 (2012) 64–72".
2) M. T. Sorour, F. Abdelrasoul and W. A. Ibrahim worked on the topic "Phenolic wastewater treatment" by using i)Activated sludge (A.S),ii) Granular activated carbon (A.C) iii) Activated sludge plus activated carbon (A.S + A.C) ,which showed (a)The A.S + A.C system gave the highest COD and phenol percentage removal comparing with the other two systems.(b) Increasing the influent phenol concentration decreased the COD and phenol removal efficiency.(c) Increasing flow rate decreased the COD and phenol removal efficiency for all systems.(d) Increasing the influent

phenol concentration results in increasing phenol toxicity for A.S system. This work had been published in journal “Tenth International Water Technology Conference, IWTC10 2006, Alexandria, Egypt 1127”.

3) G.Vijayaraghavan, T.Sivakumar, and A.Vimal Kumar worked on the topic “Application of plant based coagulants for waste water treatment” by using Nirmali seeds (Strychnospotatorum), Moringa oleifera, Tannin and Cactus. which showed these natural coagulants are highly effective for treatment of waters with low turbidity but may not be feasible in the case of wastewaters with extreme pH. Utilization of these coagulants represents important progress in sustainable environmental technology as they are renewable resources and their application improves the quality of life for under developed communities. This work had been published in journal “International Journal of Advanced Engineering Research and Studies 1 (2011)88-92”.

4) Pratarn Wongsarivej and Pornsiri Tongprem worked on the topic “Phenolic waste water treatment in three phase fluidized bed reactor” by using Activated carbon which showed Comparison of phenolic adsorption under five different adsorbents (a)fresh GAC, (b)fresh Fe/GAC,(c)1st reused GAC,(d)1st reused Fe/GAC, (e)2nd reused Fe/GAC, have been carried out. The result shows that both fresh GAC and Fe/GAC gave the better results than reused GAC and reused Fe/GAC, respectively. The adsorption followed pseudo second -order kinetics. This work had been published in “Engineering Journal : Volume 13(2009)57-59”.

5) E-S.Z. El-Ashtoukhy, Y.A.El-Taweel, O. Abdelwahab ,and E.M.Nassef worked on the topic “Treatment of Petrochemical Wastewater Containing phenolic Compounds by Electro coagulation” by Using a Fixed Bed Electrochemical Reactor with a fixed

bed anode made of randomly oriented Al raschig rings packed in a perforated plastic basket located above the horizontal cathode. The study revealed that the optimum conditions for the removal of phenolic compounds were achieved at current density = 8.59 mA/cm^2, pH = 7, NaCl concentration = 1 g/L and temperature of 25°C. Remarkable removal of 100% of phenol compound after 2 hrs can be achieved for 3 mg/L phenol concentration of real refinery wastewater. The new anode design of electro coagulation cell permits high efficiencies with lower energy consumption in comparison with other cell design used in previous studies. This work had been published in “International Journal of Electrochemical Science 8 (2013) 1534 – 1550”.

6) Somayeh Golbaz , Ahmad Jonidi Jafari , Mohammad Rafiee and Roshanak Rezaei Kalantary worked on the topic “Removal of phenol, Chromium, Cyanide ,by coagulation /precipitation process” using Ferric chloride($FeCl_3$) as a coagulant. This study showed that (a) Conventional coagulation efficiently removed Cr^{+6}; however, coagulation displayed a relatively poor removal of cyanide. In the case of phenol, insignificant removal efficiency was also observed. (b)Enhanced coagulation outperformed conventional coagulation in terms of Cr^{+6}, and phenol removal was also slightly improved. (c) Coexisting CN ions slightly inhibited Cr^{+6} removal, while chromium was simultaneously removed with the phenol containing wastewater. (d) Presence of chromium promoted the removal performance of phenol to some extent. Phenol could be oxidized in the presence of Cr^{+6}. Hexavalent chromium vice versa could be efficiently reduced to Cr^{+3} ions in the existence of phenol, and (thus) could be precipitated as chromium hydroxide, $Cr(OH)_{3.}$ (e) Statistical analysis revealed that precipitation performance was augmented in the process of treating synthetic waste

water containing both Cr^{+6} ions & phenol. This work had been published in "Chemical Engineering Journal 253 (2014) 251–257".

7) Ihsan Habib Dakhil worked on the topic "removal of phenol present in industrial waste water", Using Sawdust as an adsorbent. This study showed the optimum conditions for the removal of phenol within the experiment range of variables studies were 130 mg/L of initial phenol concentration, 0.82 gm of adsorbent dose, natural pH value of 6.7 and 120 min of contact time. Under these conditions the maximum removal efficiency was 91.6%. This work had been published in "Research Inventy: International Journal of Engineering and Science Vol.3, Issue 1 (May 2013), PP 25-31".

8) Mr. B. C. Meikap and Dr. G. K. Rot worked on the topic "Removal of phenolic Compounds from Industrial Waste Water" Using Semi-fluidized Bed Bio-Reactor. This work showed that the immobilized semi-fluidized bed bioreactor is, no doubt, a novel and efficient appliance, which can be adopted for the treatment of industrial waste water containing phenolic compounds even at lower concentration. A proper choice of immobilized culture, careful consideration of various design parameters for a semi-fluidized bed bioreactor will make treatment process cost effective in the long run. This work had been published in journal "Journal of the 1PHE, India, Vol. 1997, No. 3".

9) Hamidreza Farajnezhad & Parvin Gharbani worked on the topic “Coagulation treatment of waste water in petroleum industry” using Poly Aluminum Chloride and Ferric Chloride as a coagulant. This study showed that under optimal conditions of process parameters, a coagulant dose of 10 mg/L was efficient to remove 78 and 88% of the effluents color by ferric chloride and PAC, respectively. The best colour removal was achieved at dose concentration of 10 mg/L and pH =7. This work had been published in journal “IJRRAS 13 (1) October 2012”.

10) C R Girish and V. Ramachandra Murty worked on the topic “Adsorption of Phenol from waste water using locally available adsorbents like activated carbons from agricultural by-products such as coconut shell, husk, shells, rice husk seed coat, stone, kernels and peels of various agricultural products, palm oil empty fruit product, miscellaneous agricultural wastes like bark, wooden, roots and other products like straw, fibers, bagasse, hulls. This study showed that these agricultural materials have equivalent or even more adsorption capacity to activated carbon. Comparing different adsorbent has high difficulty since different parameters are taken into consideration for evaluating the overall performance of the adsorbent**.** Finally, if the adsorbent comes out with very good efficiency for the treatment of wastewater containing phenol and its compounds, then it can be successfully commercialized to industrial scale which will be beneficial to the society in future. This work had been published in journal “Journal of Environmental Research and Development Vol. 6 No. 3A, Jan-March 2012”.

11) Maria Tomaszewska, S ylwia Mozia, and Antoni W. Morawski worked on the topic "Removal of organic matter by coagulation enhanced with adsorption". A PAX XL-69 polyaluminum chloride was used as a coagulant & powedered activated carbon as adsorbent. This study showed that 1) Coagulation of solutions containing phenol without the addition of PAC is less effective in comparison with the adsorption coagulation integrated system. Phenol remains in solution. 2) The combination of adsorption and coagulation allows the removal of PAC with adsorbed organics from solution. The additional advantage of such a process is greater effectiveness of HAS removal in comparison with adsorption conducted without coagulation.3) Coagulation enhanced with adsorption on PAC has better results when coagulation is preceded by adsorption than when the two processes are carried out simultaneously. This study had been published in the journal "Desalination 161 (2004) 79-87"

After detailed study of literature work we have seen that many coagulants and adsorbents have been used for the removal of waste water. Generally coagulation and adsorption process used as separate process, but in some work we have seen that combined effect of coagulation and adsorption showed increased efficiency of phenol removal. So we can conclude that combined effect of both process will give better phenol removal, and my research work will follow the same trend of coagulation followed by adsorption process by using **$FeCl_3$** and **$Al_2(SO_4)_3$** as a coagulant and treated **fly ash** as an adsorbent.

Chapter-4

EXPERIMENTAL WORK

MATERIALS & METHODOLOGY

4.1 Adsorption of Synthetic phenol

4.1.1 PREPARATION OF SYNTHETIC PHENOL

MATERIALS REQUIRED

1. Phenol(C_6H_5OH)
2. Distilled Water

PROCEDURE

100 ppm stock solution was prepared by dissolving 100 mg of phenol in 1000 ml of distilled water.

Then 10 or 20 ppm working standard solution was prepared by appropriate dilution of standard stock solution.

4.1.2 TREATMENT OF FLY ASH

MATERIALS REQUIRED

1. Raw fly ash (New Kashipur Thermal Power Plant)
2. Calcium Hydroxide ,$Ca(OH)_2$
3. Distilled Water

PROCEDURE

1. 5 g Calcium Hydroxide was mixed in 100 ml of distilled water.
2. 17 g raw fly ash was measured.
3. Fly ash mixed in Calcium Hydroxide solution and stirred for 3 hour.
4. Fly ash separated from the suspension by filtration.
5. Finally dried at 70^oC for 24 hour and collect it carefully in container.

After treatment with $Ca(OH)_2$ surface roughness of fly ash changed significantly. This change includes wearing of asperities and particles cracking. Pores and cavities of fly ash increased significantly. Furthermore, the pores on the surface of the adsorbent are highly heterogeneous. The heterogeneous pores and cavities provides a large exposed surface area for the adsorption of phenol,(Chowdhury and Saha).

RAW FLYASH

TREATED FLYASH

4.1.3 Adsorption of Phenol

1. 10 ppm, 100 ml phenol solution was prepared from stock solution of synthetic phenol.

2. Four different 250 ml conical flasks was taken & transferred 100 ml, 10 ppm synthetic phenol in conical flask.

3. 20 mg,50 mg, 100 mg & 200 mg fly ash were measured and mix in the synthetic phenol.

4. Conical flask placed in shaker at 120-140 rpm for 90 min.

5. Sample was taken after 45 min,60 min, 75 min, and 90 min.(sample collection should be very carefully by the sucker with the help of tip, so that no amount of adsorbent come out with supernatant.)

6. Collected sample was placed in centrifuge for 15-20 min at the speed of 10000 rpm.

7. Sample was collected from centrifuge and absorbance was measured with the help of UV-VIS Spectrophotometer at wavelength of 270 nm.

This process has been applied for different parameters variations like adsorbent dose(20 ,50,100,200 mg),temperature(25,30,35,40&45^{o}C),pH(4,6,8,10),Phenol concentration(5,10,15 ppm), and for different shaker speed(80,100,125,150 rpm). **The optimum adsorption parameter was found at adsorbent dose of 100 mg,10 ppm concentration, pH 4,shaker speed of 150 rpm at 45^{o}C temperature.**

4.2 Characterization of Phenolic Waste Water

1. Procurement of phenolic waste water from Amit petro product on 1^{st} Feb, 2016.

2. Characterization of phenolic waste water by computing **pH, TSS, TDS, BOD, COD, and phenol concentration**.

4.2.1 pH

Industrial sample was taken in a beaker and pH was measured by putting pH pen in the sample and reading was noted down. pH comes equal to **4.1**.

Measurement of pH by pH pen

4.2.2 Total Suspended Solid (TSS)

TSS of a water or wastewater sample is determined by pouring a carefully measured volume of water (typically one litre; but here less amount is taken because of less amount of sample) through a pre-weighed filter of a specified pore size, then weighing the filter again after drying to remove all water. The gain in weight is a dry weight measure of the particulates present in the water sample expressed in units derived or calculated from the volume of water filtered (typically milligrams per litre or mg/L).

$$\mathbf{TSS} = A_2 - A_1$$

where, A_1=Initial weight of dried filter paper

A_2=Final weight of wet filter paper (oven dried)

Here, TSS value comes equal to **4100 mg/L.**

4.2.3 Total Dissolved Solid

The two principal methods of measuring total dissolved solids are gravimetric analysis and conductivity**.** Gravimetric methods are the most accurate and involve evaporating the liquid solvent and measuring the mass of residues left. This method is generally the best, although it is time-consuming. TDS is expressed in mg/L.

$$\mathbf{TDS} = \mathbf{A_2 - A_1}$$

Where, A_1=Initial weight of dried beaker

A_2=Final weight of dried beaker (oven dried)

Here, TDS value comes equal to **11000 mg/L.**

4.2.4 Biological Oxygen Demand

Demand Oxygen Measurement

MATERIALS REQUIRED

1)Manganous Sulphate Solution
Dissolve 364g $MnSO_4.H_2O$ in 1000 ml Distilled water.

2) Alkaline-Iodide- Azide Solution

Take 500g of sodium hydroxide and 150g of Sodium Iodide and dissolve it in 950 ml distilled water. Dissolve 10g of Sodium Azide (NaN_3) in 40 ml of distilled water and add this with constant stirring to the cool alkaline iodide solution prepared before. The solution should not give colour with starch solution when diluted and acidified. Stored in dark.

3) Sodium Thiosulphate Solution (0.025N)

Weigh 6.025g of Sodium Thiosulphate ($Na_2S_2O_3.5H_2O$) and dissolved it in distilled water and make up to 1000 ml.

4) Starch Indicator

Weigh 0.5 g of starch and dissolve in 100 ml of hot Distilled water. To preserve the starch indicator add 0.2 g of Salicyclic acid as preservative.

5) Standard Potassium dichromate (0.25 N)

1.225 g Potassium dichromate ($K_2Cr_2O_7$) in 100 ml distilled water.

PROCEDURE

1) The sample is collected in a BOD bottle (300 ml capacity) taking care to avoid any bubbling.

2) 1 ml $MnSO_4$ + 1 ml alkali-iodide-azide is added to the bottle , submerging the pipette to the liquid level.

3) The stopper is placed carefully to exclude air bubble and mixed the solution by inverting it repeatedly for 15 min. The precipitate is allowed to settle.

4) Then 1 ml of conc. H_2SO_4 is added, bottle is closed and mixed properly.

5) 50 ml of the content of the bottle is titrated with Sodium thiosulphate using Starch as an indicator .At the end point the blue colour turns colourless. Reading noted down.

Calculation

Demand Oxygen in mg/L= ml of titrant * normality *8 * 1000*$V_1/v_2(v_1-v)$

Where, V_1=Volume of BOD bottle in ml

V_2=Volume of the content titrated in ml

V_3= Volume of MnSO4 and iodide azide solution. i.e 1+1=2 ml.

BOD MEASUREMENT

MATERIALS REQUIRED

1)Phosphate buffer solution

Dissolved 0.85 g KH_2PO_4 +2.17 g K_2HPO_4+ 3.3 g $Na_2HPO_4.7\ H_2O$+0.17 g NH_4Cl in 100 ml distilled water. Maintan pH=7.2, with the help of NaOH and HCl.

2) Magnesium Sulphate solution

Dissolved 2.25 g $MgSO_4$ in 100 ml distilled water.

3) Calcium Chloride solution

2.75 g $CaCl_2$ (anhydrous) in 100ml distilled water.

4) Ferric Chloride solution

Dissolved 0.25 g $FeCl_3.6H_2O$ in 1000 ml distilled water.

Preparation of dilution water

1) Aeration:

Required volume of distilled water aerated in glass jar for 2 days ,temperature maintained 27°C. Add 1ml of Phosphate buffer + 1 ml $MgSO_4$ + 1 ml $CaCl_2$+ 1 ml $FeCl_3$ is added to 1 L distilled water and mixed well.

Water Aeration

PROCEDURE

1)60 ml sample water is added to 540 ml aerated water.

2) From 600 ml diluted sample water ,300 ml was taken in a BOD bottle and initial DO was measured by Winkler's method.

3) The other 300 ml diluted sample water was taken in a BOD bottle and kept in incubator at 27°C for 3 days.

4) After incubation ,the final DO of the sample was measured.The reading was noted down.

Calculation **BOD_3(mg/L)=**D_1-D_2/F

Where, D_1= initial DO

D_2=final DO

F=dilution factor

Before addition of H_2SO_4

After addition of H_2SO_4

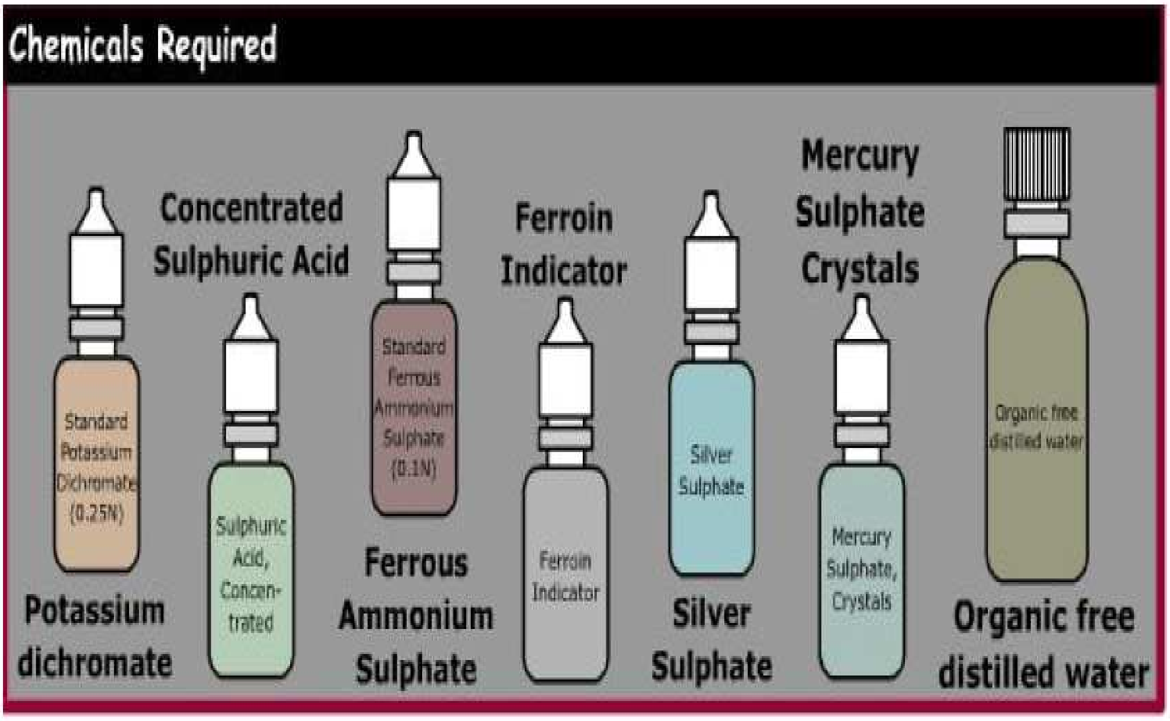
BOD value of water sample comes **1820 mg/L.**

4.2.5 CHEMICAL OXYGEN DEMAND

MATERIALS REQUIRED

Chemical required

1. Potassium dichromate
2. Sulfuric acid
3. Ferrous ammonium sulphate
4. Silver sulphate
5. Mercury sulphate
6. Ferroin indicator
7. Organic free distilled water



Apparatus required

1) COD digester

2) Burette & burette stand

3) COD vials with stand

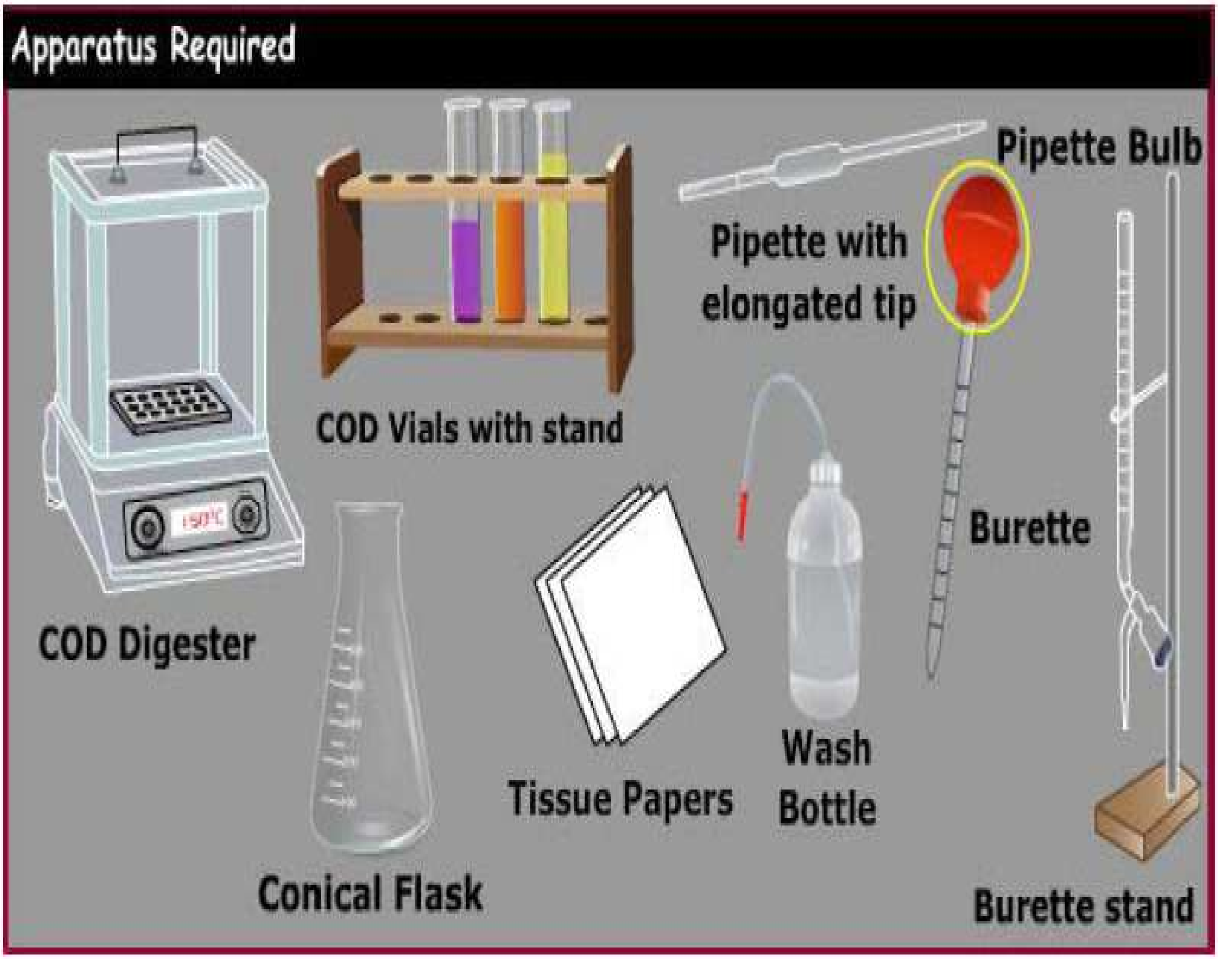
4) 250 ml conical flask (Erlenmeyer Flask)

5) Pipettes

6) Pipette bulb

7) Tissue papers

8) Wash bottle.



PROCEDURE

1. Preparation of reagents:

   - Standard Potassium Dichromate Reagent - Digestion Solution

     4.913 g of potassium dichromate was dried at 103ºC for 2 - 4 hours. 33.3g of mercuric sulphate was add to the beaker containing dried potassium dichromate. 167 ml of concentrated sulphuric acid was measured using clean dry measuring cylinder and was transferd to the same beaker. The contents was dissolved and cooled to room temperature. The contents was transferred to an 1000 ml standard flask and distilled water added to make it upto 1000ml.

   - Sulphuric Acid Reagent - Catalyst Solution

     5.5 g silver sulphate crystals was taken in a dry clean 1000 ml beaker. To this 500 ml of concentrated sulphuric acid was carefully added and was allowed to stand for 24 hours (so that the silver sulphate crystals dissolve completely).

   - Standard Ferrous Ammonium Sulphate solution

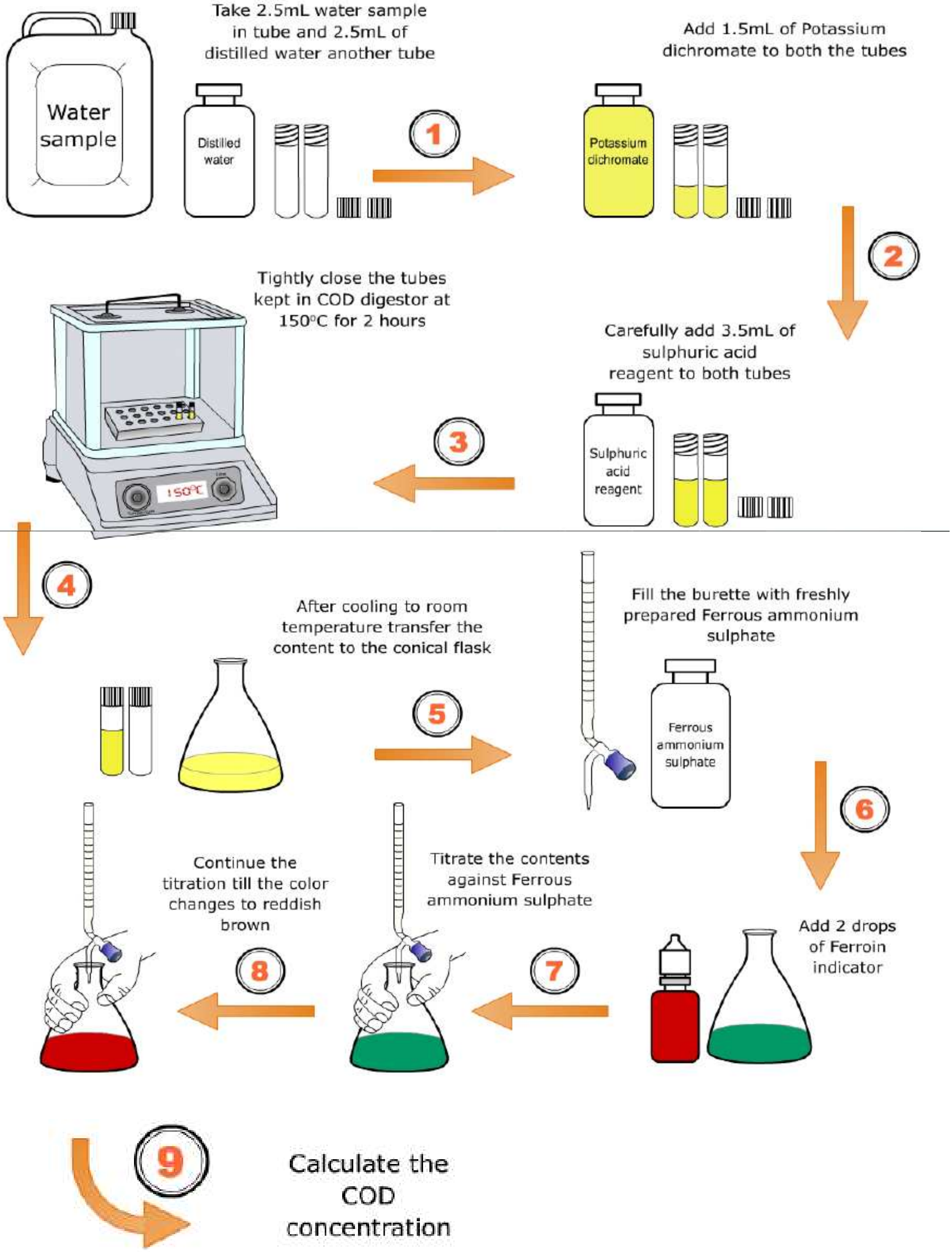
     39.2g of ferrous ammonium sulphate crystals was dissolved in 1000ml distilled water.

2. Testing of samples:

   - 3 COD vials with stopper (two for the sample and one for the blank) were taken.
   - 2.5ml of the sample was added to each of the two COD vials and the remaining COD vials was kept for blank so to this COD vial distilled water was added.
   - 1.5ml of potassium dichromate reagent - digestion solution was added to each of the three COD vials.

- 3.5 ml of sulphuric acid reagent - catalyst solution was added to each of the three COD vials.
- Tubes were capped tightly. COD Digester temperature was fixed at 150º C and the time was set for 2 hours.
- The COD vials were placed into a block digester at 150°C and were heated for two hours.
- Then the vials were removed and were allowed it to cool to the room temperature.
- The burette was filled with the ferrous ammonium sulphate solution, and was fixed to the burette stand.
- The content of the blank vial was transferred to conical flask.
- Few drops of ferroin indicator were added. The solution became bluish green in colour.
- Titration was carried out. End point of the titration was noted at the appearance of the reddish brown colour. Burette reading was noted down.
- Similar titration was carried out for the two samples and the burette readings were noted down.

PROCEDURE CHART



Take 2.5mL water sample in tube and 2.5mL of distilled water another tube

Add 1.5mL of Potassium dichromate to both the tubes

Carefully add 3.5mL of sulphuric acid reagent to both tubes

Tightly close the tubes kept in COD digestor at 150°C for 2 hours

After cooling to room temperature transfer the content to the conical flask

Fill the burette with freshly prepared Ferrous ammonium sulphate

Add 2 drops of Ferroin indicator

Titrate the contents against Ferrous ammonium sulphate

Continue the titration till the color changes to reddish brown

Calculate the COD concentration

Calculation

COD= (A-B)*N*8*1000/volume of sample

Where,

A=Burette reading for distilled water

B=Burette reading for sample.

Value of COD for sample comes **400000 mg/L.**

4.2.6 DETERMINATION OF PHENOL CONCENTRATION

MATERIALS REQUIRED

1. Phenolic sample water
2. Cuvette
3. Distilled Water
4. Tissue paper

PROCEDURE

Phenol concentration was measured with the help of UV-VIS Spectrophotometre. Phenol amount present in the sample was very high. Value of phenol concentration comes 27500 ppm.

4.3 Coagulation of phenolic waste water

MATERIALS REQUIRED

1) Alum(Aluminium Sulphate) as a coagulant
2) Ferric Chloride($FeCl_3$) as a coagulant
3) Phenolic waste water collected from industries
4) Sodium Hydroxide for pH maintain
5) Hydrochloric Acid to maintain pH.
6) Distilled Water

PROCEDURE

1)100 ml of phenolic waste water was taken in 250 ml conical flask & pH was maintained to 7 with the help of NaOH/HCl

2) Alum was added in three different amount (2,4,6 g)in three different conical flask and Ferric Chloride (10% W/V)solution was added in three different volume(5,10,15 ml) in three different conical flask.

3) Coagulants were mixed properly in phenolic waste water.

4) After that, it is allowed to settle down for 1-2 hr.

5) The supernatant was collected & the characterization was done by calculating pH, TSS, TDS, BOD, COD.

4.4 Adsorption of supernatant after coagulation

MATERIALS REQUIRED

1) Supernatant solution (collected after coagulation)

2) Fly ash

3) NaOH

4) HCl

PROCEDURE

1)100 ml supernatant solution after coagulation was collected.

2) Take three 250 ml conical flask & put 100 ml supernatant solution.

3) Maintain concentration of 10 ppm and pH 4 of supernatant solution in conical flask.

4) Measure 100 mg fly ash and mix in the supernatant solution.

5) Put conical flask in shaker at 150 rpm for 90 min at 45^{o}C.

6) Take sample after 45 min,60 min, 75 min, and 90 min.(sample collection should be very carefully by the sucker with the help of tip, so that no amount of adsorbent come out with supernatant.)

7) Place that collected sample in centrifuge for 15-20 min at the speed of 10000 rpm.

8) Collect sample from centrifuge and measure absorbance with the help of UV-VIS Spectrophotometer at wavelength of 270 nm.

4.5 Characterization of supernatant after adsorption

Supernatant was collected after adsorption by filtration with filter paper and characterization was done by measuring pH and determining TSS, TDS, BOD, COD & phenol concentration.

CHAPTER-5

RESULT & DISCUSSION

5.1 Phenol standard curve

Peak at wavelength of 270 nm is highest, i.e.at this wavelength number of particles of phenol is more. So, at this wavelength we find the absorbance of different phenol concentration to draw the standard curve. Table shown below shows the value of absorbance at 270 nm of different phenol concentration.

Phenol concentration(ppm)	Absorbance(at 270 nm)
2.5	0.014
5	0.048
10	0.148
50	1.040

As the above table didn't give the relation between concentration and absorbance. So, to find this relation we have to draw a standard curve between concentration and absorbance. From there we find the value of R^2=0.9936.

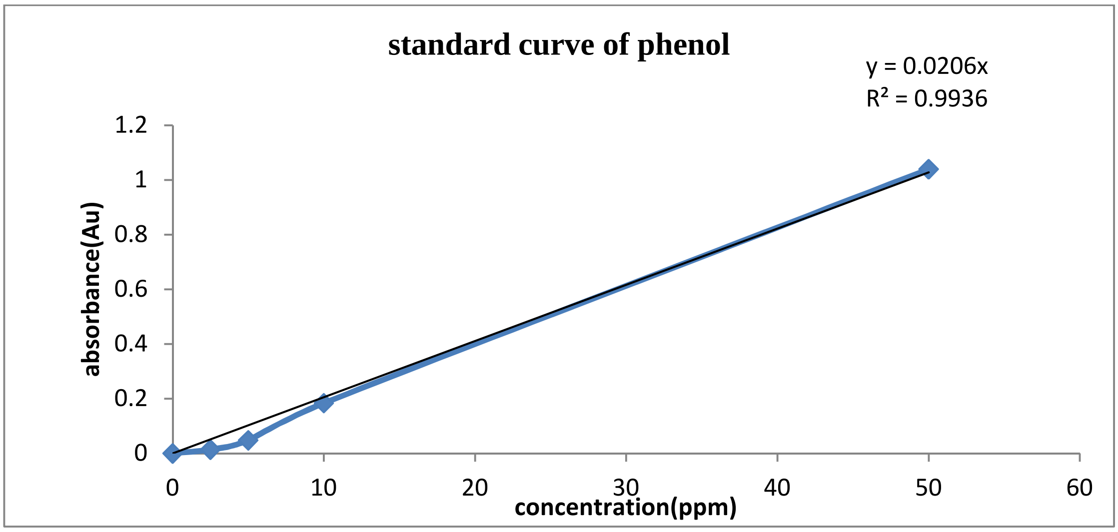


Fig 1: Phenol standard curve, absorbance vs concentration

Above curve gives the relation, **Y=0.020X**

Where,Y= Value of absorbance

X= Value of concentration

5.2 Adsorption of synthetic phenol

Adsorption study of synthetic phenol on fly ash have been done by varying various parameters like *adsorbent dose, temperature, pH, Phenol concentration, and shaker speed.*

5.2.1Variation of adsorbent dose

Firstly percentage removal of phenol was calculated by varying dose of adsorbent keeping other parameters (temperature, pH, phenol concentration, and shaker speed) constant.

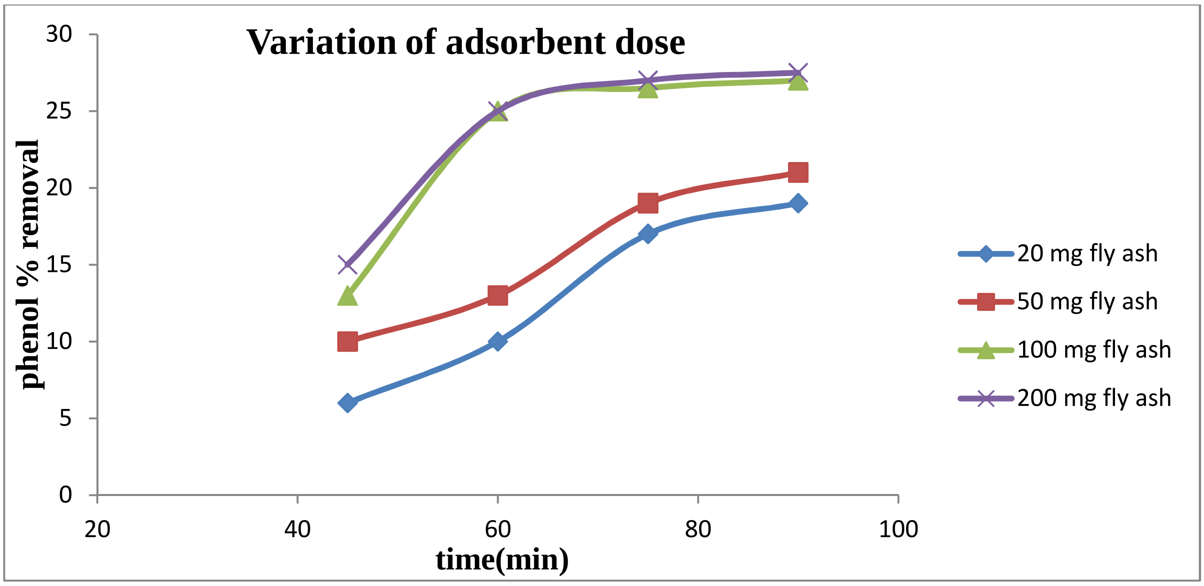


Fig 2: shows percentage removal of phenol on different adsorbent (fly ash) dose.

Above graph shows the % removal of phenol with respect to different adsorbent dose in different time interval. Study shows that percentage removal increases with increasing time in all three adsorbent dose. Maximum percentage removal shows in adsorbent dose of 100 mg at the time interval of 90 min .i.e about 27.5 %. As adsorbent dose increases surface area for adsorption also increases, simultaneously percentage removal of phenol not increasing (almost constant). Active site of fly ash saturated by the phenol group, so the percentage removal could not be increases.

5.2.2 Variation of temperature

In second step percentage removal of phenol was calculated by varying temperature and considering other parameters (adsorbent dose, pH, phenol concentration, and shaker speed) constant.

Temperature (^{o}C)	Absorbance	Concentration	% removal
25	0.144	7.2	28
30	0.140	7	30
35	0.131	6.55	34.5
40	0.126	6.3	37
45	0.118	5.9	41

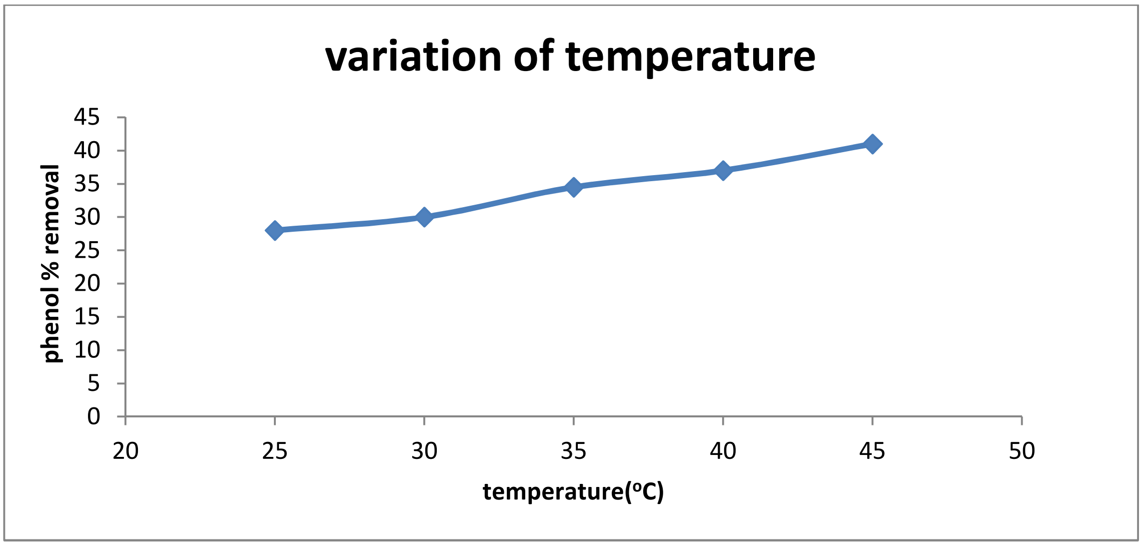


Fig 3: percentage removal of phenol on different temperature

Above graph shows the % removal of phenol with respect to different temperature value. Percentage removal increases with increasing temperature. Maximum percentage removal shows at 45^{o}C .i.e about 41.0 %.As temperature increases energy also increases and bonding between fly ash molecules break. Due to this adsorption capacity of fly ash increases as temperature increases.

5.2.3 Variation of pH

In third step percentage removal of phenol was calculated by varying pH of phenol (with NaOH & HCl) and considering other parameters (adsorbent dose, temperature, phenol concentration, and shaker speed) constant.

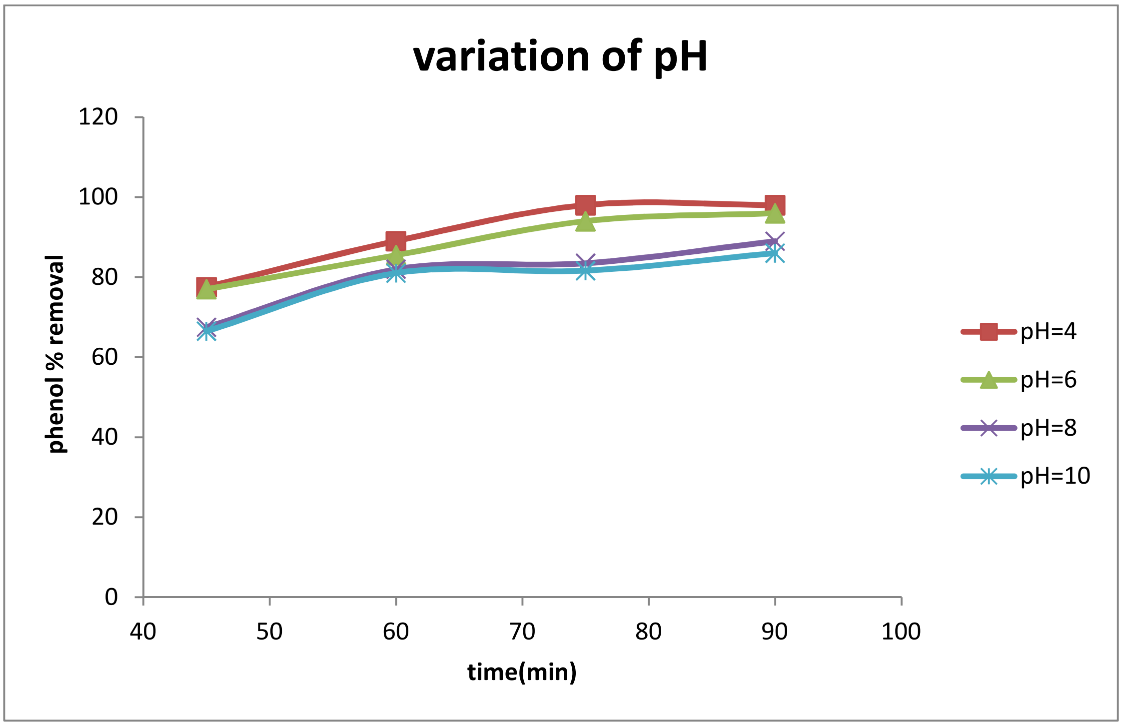


Fig 4: percentage removal of phenol on different pH value

Above graph shows the % removal of phenol with respect to different pH in different time interval. Percentage removal increases with increasing time in all four pH values. As phenol solution is acidic in nature. So, the maximum percentage removal should be in the acidic region and we are seeing that maximum percentage removal shows in pH value 4 and .i.e about 98 %.

5.2.4 Variation of phenol concentration

In this step percentage removal of phenol was calculated by varying phenol concentration and considering other parameters (adsorbent dose, pH, temperature, and shaker speed) constant.

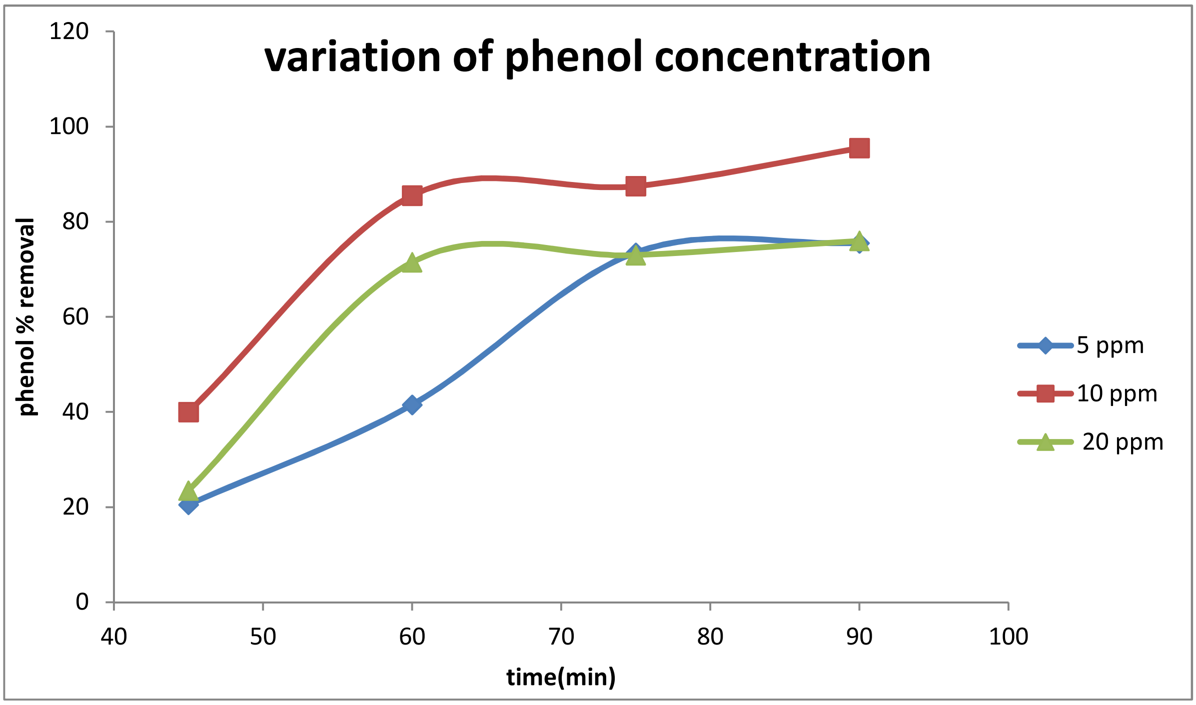


Fig 5: percentage removal of phenol on different phenol concentration

Above graph shows the percentage removal of phenol with respect to different phenol concentration in different time interval. Percentage removal increases with increasing time in all concentration values. Here maximum percentage removal shows in concentration value 10 ppm and .i.e about 95.5 %.In lower value of phenol concentration amount of phenol present is very less and in higher concentration amount of phenol present is very high and we are applying fixed amount of adsorbent dose that’s why percentage removal in 10 ppm is maximum.

5.2.5 Variation of shaker speed

In last step percentage removal of phenol was calculated by varying shaker speed and considering other parameters (adsorbent dose, pH, phenol concentration, and temperature) constant.

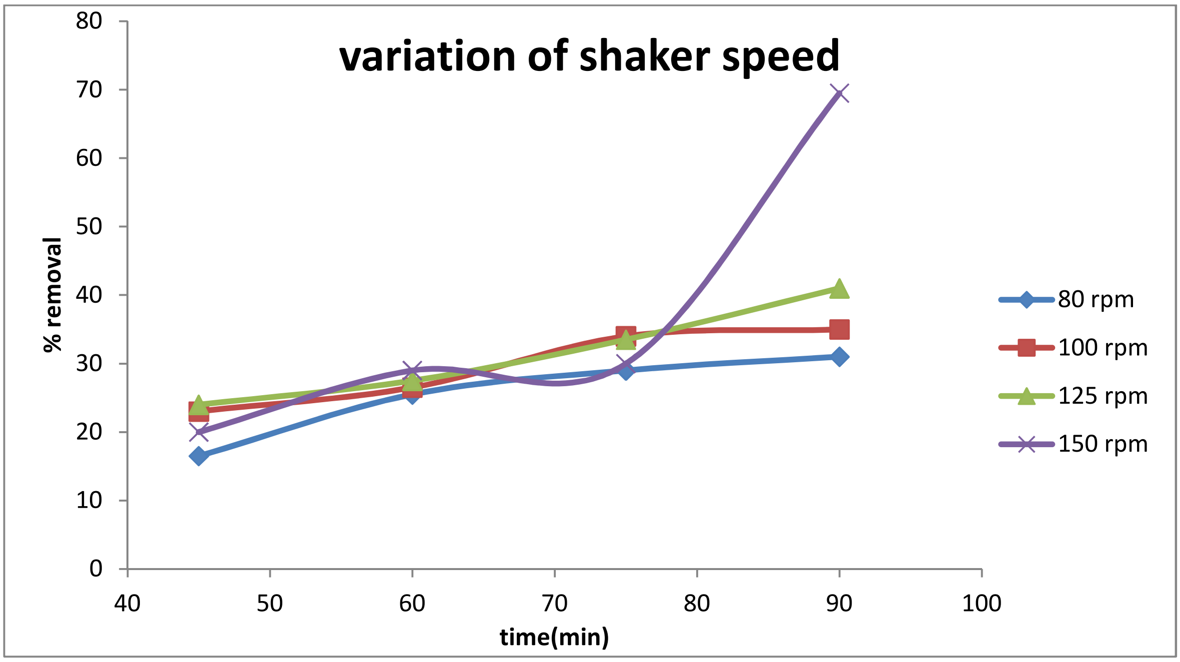


Fig 6: percentage removal of phenol on different shaking speed

Above graph shows the % removal of phenol with respect to different shaker speed in different time interval. Percentage removal increases with increasing time in all shaker speed values. Here maximum percentage removal shows in shaker speed of 150 rpm and .i.e about 69.5 %.At higher rpm value mechanical force increases and due to increase in force interaction between the fly ash and phenol solution is more, consequently phenol removal is more.

By taking all parameter variation into account we have seen that the optimum condition of adsorption of 10 ppm phenol concentration shown at shaker speed of 150 rpm ,at 45^{o}C ,at pH value of 4 and adsorbent dose of 100 mg fly ash at the time interval of 90 min .

5.3 Characterization of supernatant

a) after coagulation with Aluminium Sulphate

Industrial phenol sample was collected and characterization was done. value came pH=4.1, TSS=4100 mg/L, TDS=11000 mg/L, BOD=1820 mg/L, COD=400000 mg/L.

After coagulation with Aluminium Sulphate percentage removal of BOD, COD, pH, and phenol concentration are shown below in graph.

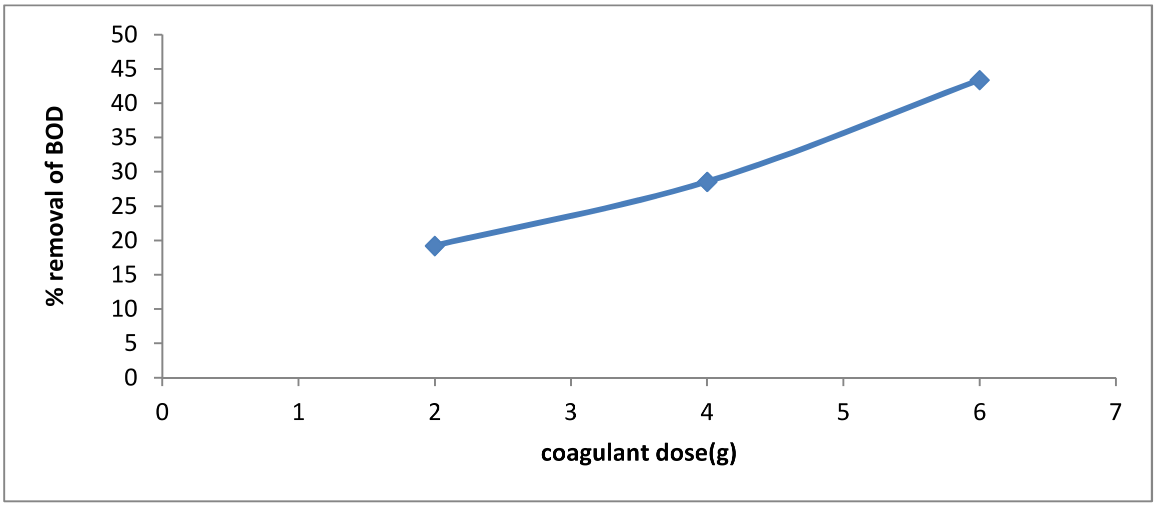


Fig 7: percentage removal of BOD after coagulation with different amount of $Al_2(SO_4)_3$ (2g,4g,6g).

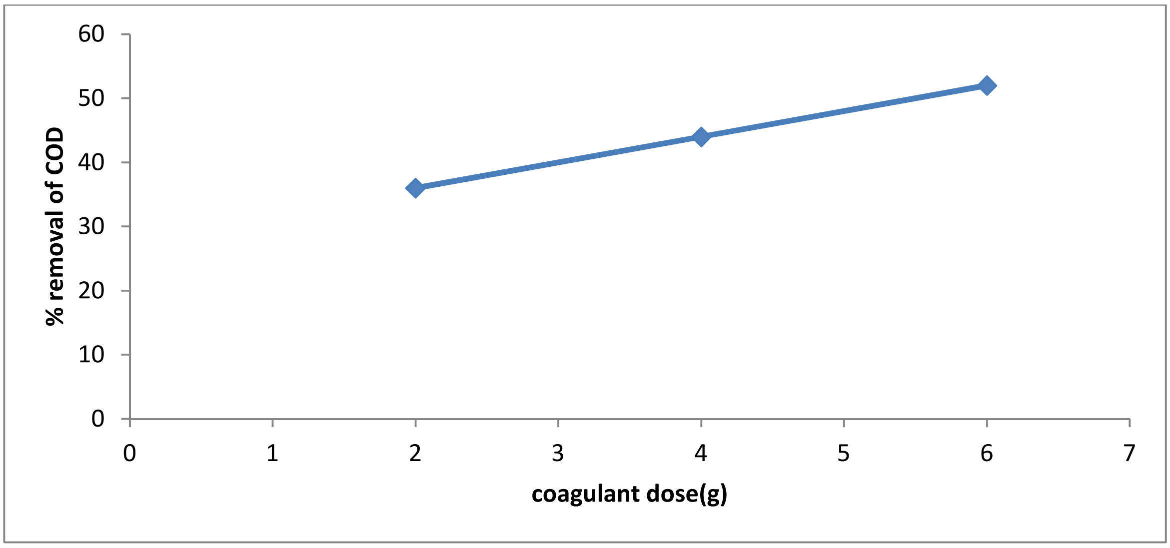


Fig 8: percentage removal of COD after coagulation with different amount of $Al_2(SO_4)_3$ (2g,4g,6g).

Coagulant dose ⟹	**Initial**	**2 g**	**4 g**	**6 g**
TSS(mg/L)	4100	1700	5250	18800
TDS(mg/L)	11000	28700	44000	69150
pH	4.1	3.9	3.6	3.6

Value of TSS decreased in 2 g coagulant dose but increased in 4 g & 6 g .The possible reason of this effect should be amount of coagulant particles present in supernatant.

Value of TDS increased in every coagulant dose. The possible reasons should be amount of coagulant particles present in supernatant and human error during filtration.

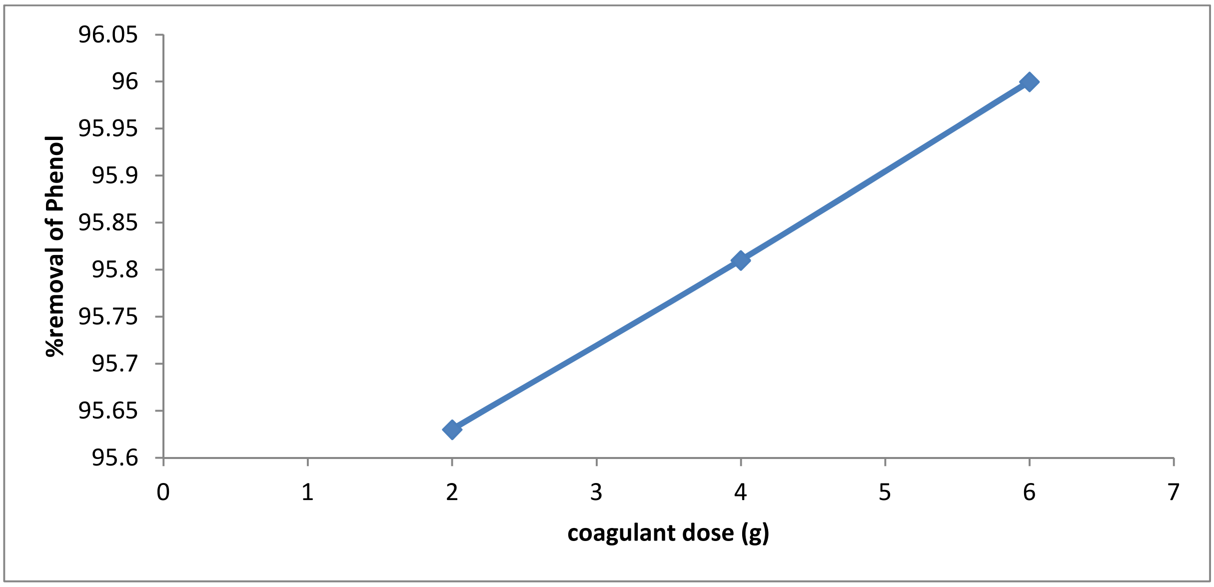


Fig 9: percentage removal of phenol after coagulation with different amount of $Al_2(SO_4)_3$ (2g,4g,6g).

Percentage removal of Phenol by Aluminium Sulphate shown very good result. It is around 95-96%. In 6 g coagulant dose percentage removal is best i.e about 96% which is maximum.

b) Characterization of supernatant after adsorption

After coagulation (with Aluminium sulphate) the remaining phenol in supernatant can be adsorbed by using fly ash (100 mg). Percentage removal of BOD, COD, and phenol are shown below in graph.

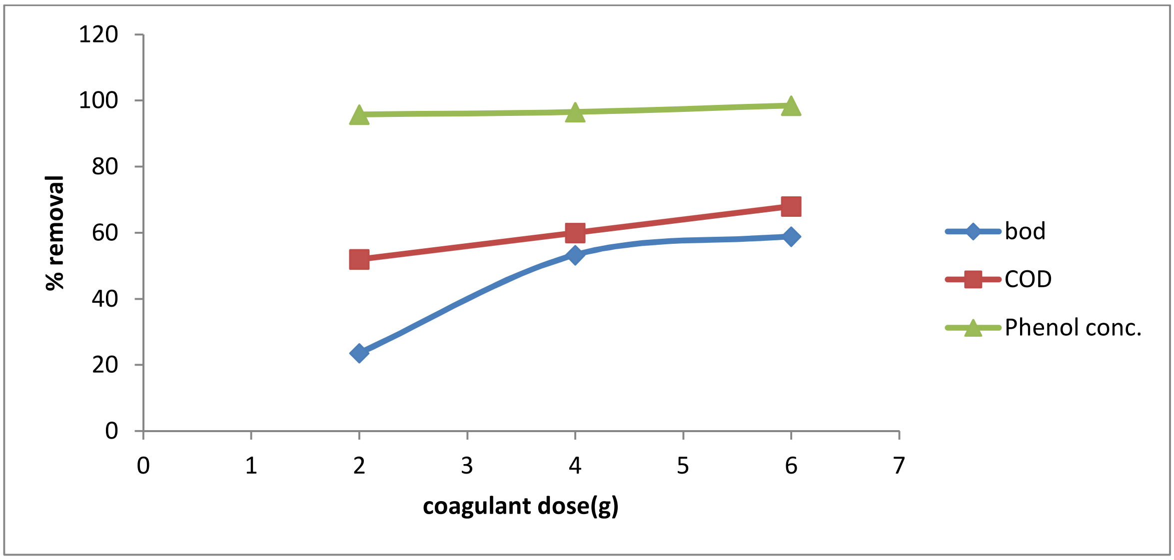


Fig 10: percentage removal of BOD, COD and phenol after adsorption (with fly ash) of treated water by coagulation (with Aluminium sulphate)

Percentage removal of Biological Oxygen demand, Chemical Oxygen demand and Phenol concentration increased. BOD % removal goes up to 59.89 %.COD % removal increased to 68%. Percentage removal of Phenol concentration reached 98.51 %.

Coagulant dose ⇨	**initial**	**2 g**	**4 g**	**6 g**
TSS(mg/L)	4100	2075	1920	3205
TDS(mg/L)	11000	25125	41720	53833.5
pH	4.1	3.4	3.0	2.7

Value of TSS decreases and TDS increases. pH values also decreased.

c) Adsorption (with fly ash) preceded by coagulation (with Aluminium Sulphate)

Optimum condition of adsorption of synthetic phenol are (Adsorbent dose of 100 mg, temp= 45^{o}C, pH= 4, phenol concentration= 10 ppm & shaker speed of 150 rpm).

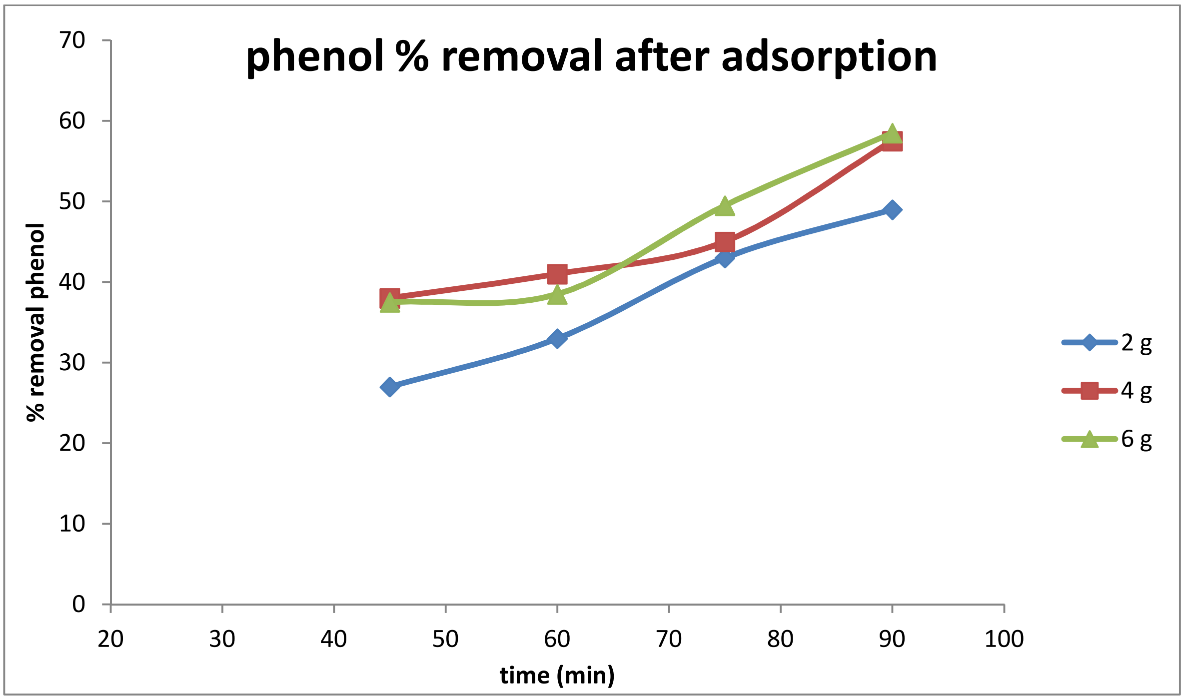


Fig 11: variation of phenol % removal after adsorption with fly ash on optimum condition of adsorption preceded by coagulation with different amount of Aluminium Sulphate

Percentage removal of phenol increased after adsorption of treated water with 6 g coagulant dose. Maximum removal comes 58.5% in case of 6 g coagulant dose at the time interval of 90 min.

5.3.1 Characterization of Phenol

a) After coagulation with Ferric Chloride

After coagulation with Ferric Chloride percentage removal of COD, BOD, and phenol concentraion are shown below in graph.

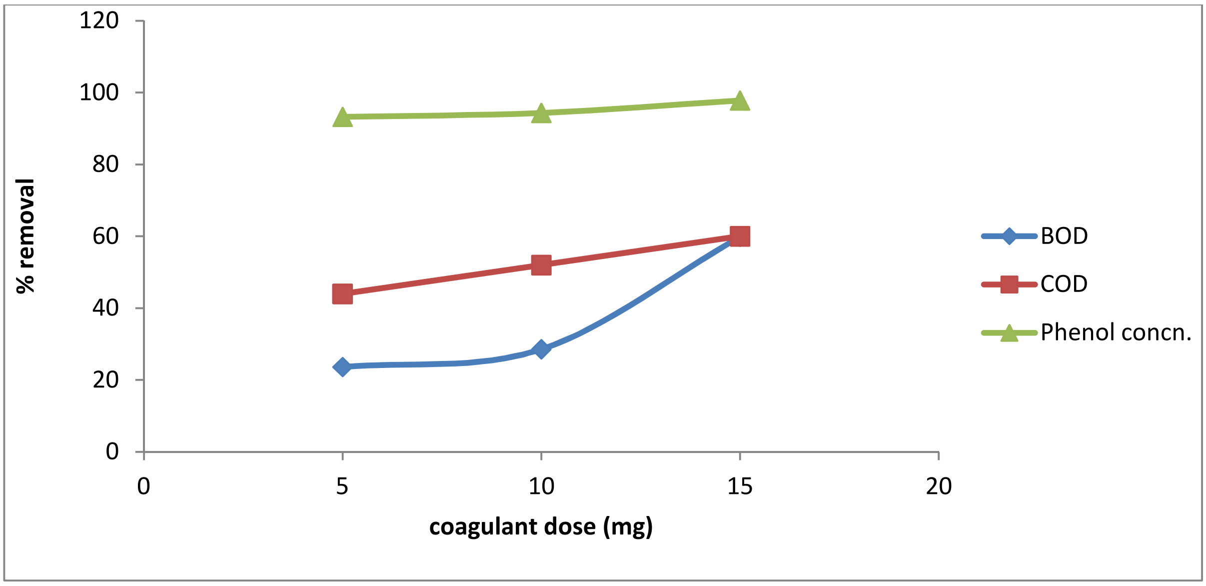


Fig12: percentage removal of BOD, COD, and phenol (100 ml) after coagulation with Ferric Chloride(5mg,10mg,15mg)

Percentage removal of BOD, COD, and phenol concentration was seen maximum in 15 mg of coagulant dose. Which is 59.89 %, 60 %, 97.81 % respectively.

Coagulant dose ⇨	**initial**	**5 mg**	**10 mg**	**15 mg**
TSS(mg/L)	4100	1375	35	275
TDS(mg/L)	11000	15635	32250	12725
pH	4.1	5.8	5.5	5.3

b)Characterization of supernatant after adsorption

Characterization of supernatant done **after adsorption (with fly ash)** of supernatant collected **after coagulation (with Ferric Chloride).** Percentage removal of BOD, COD & phenol are shown below in graph

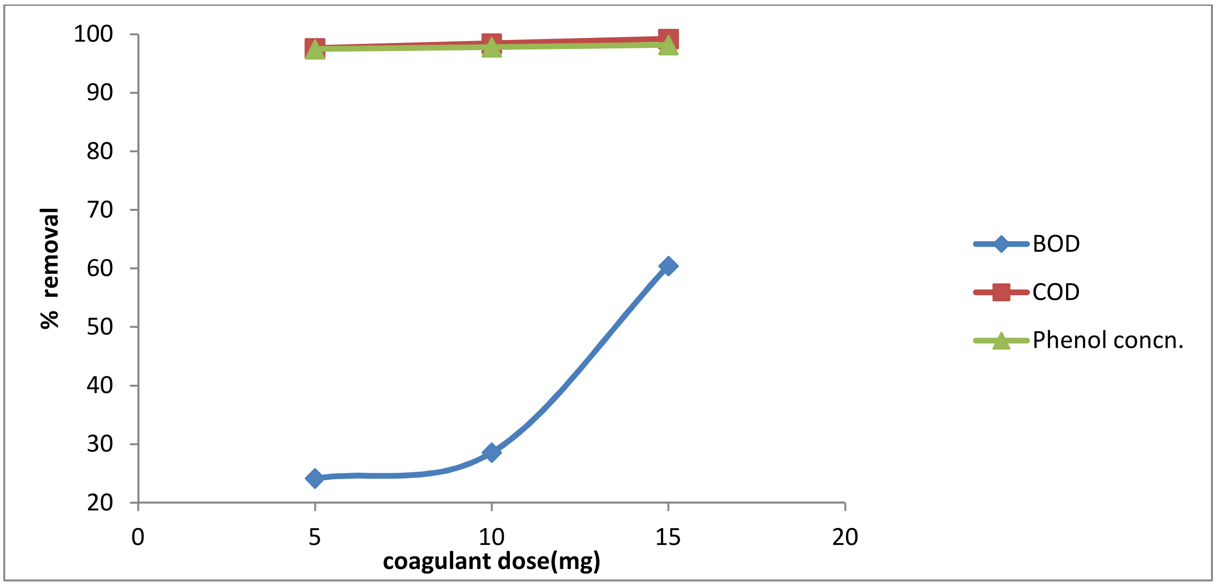


Fig13: percentage removal of BOD, COD and phenol after adsorption (with fly ash) of treated water by coagulation (with Ferric chloride).

Percentage removal of Biological Oxygen demand, Chemical Oxygen demand and phenol concentration increased. BOD % removal goes up to 60.43 %.COD % removal increased to 99.2%. Percentage removal of phenol concentration reached 98.18 %. Two graph are almost coincide because values lies between 97-99%.

Coagulant dose ⇨	**initial**	**5 mg**	**10 mg**	**15 mg**
TSS(mg/L)	4100	679	1124	587
TDS(mg/L)	11000	21672.5	20645	18540
pH	4.1	8.3	8.6	8.9

c) Adsorption of supernatant (with fly ash) preceded by coagulation of phenol (with Ferric Chloride)

Optimum condition of adsorption of synthetic phenol (Adsorbent dose of 100 mg, temp= 45^{o}C, pH= 4, Phenol concentration= 10 ppm & shaker speed of 150 rpm.)

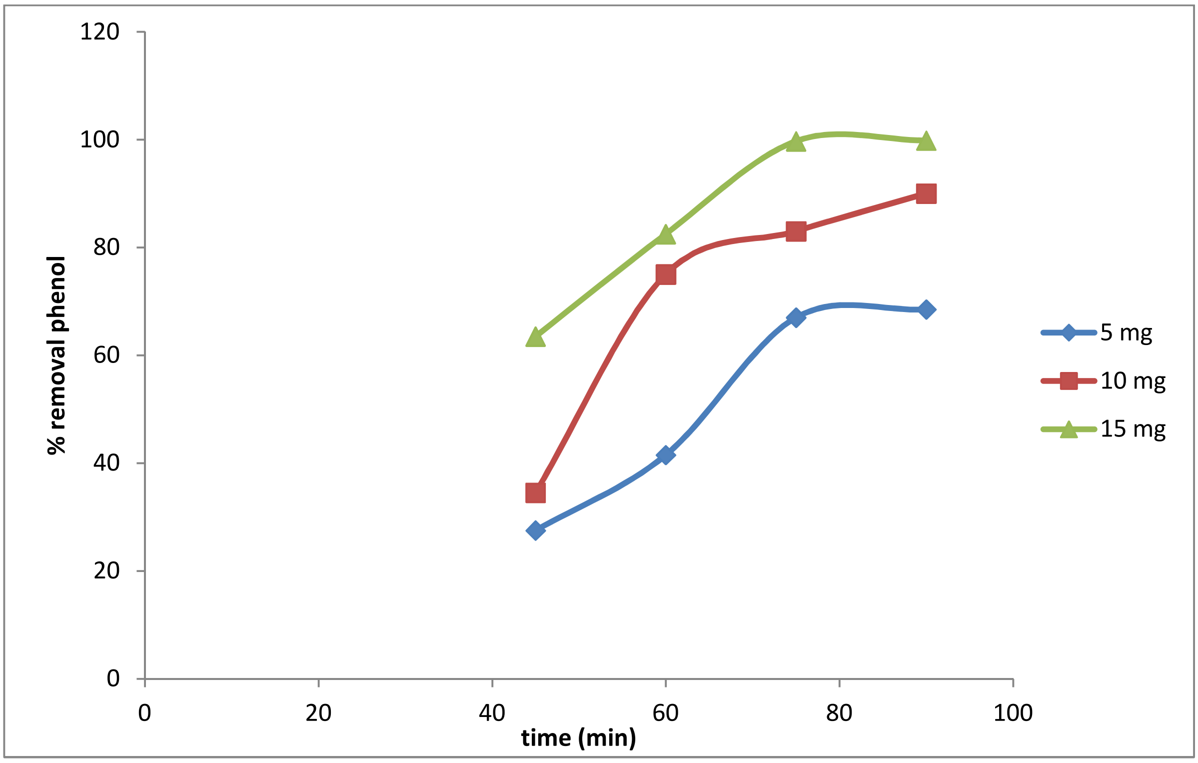
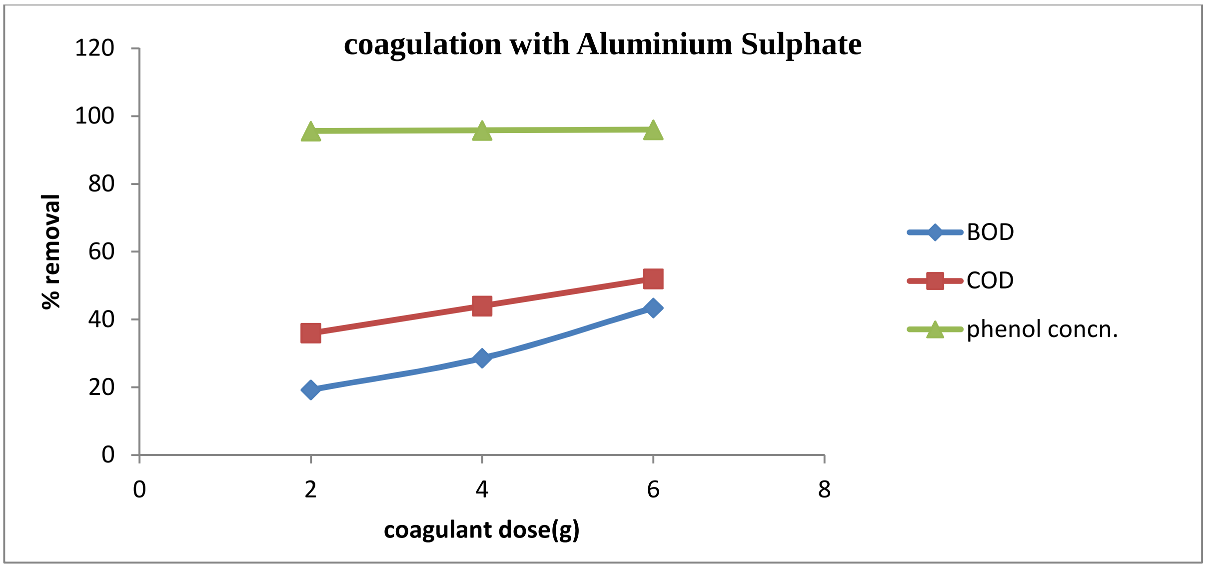


Fig 14: variation of phenol % removal after adsorption with fly ash on optimum condition of adsorption preceded by coagulation with different amount of Ferric chloride

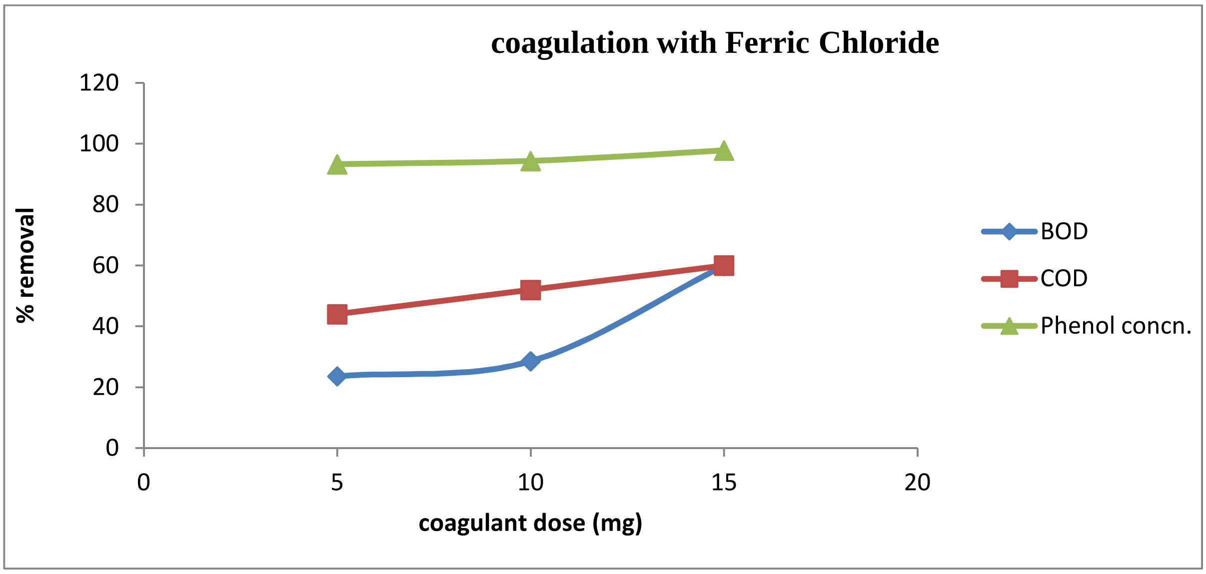
Percentage removal increased in all three amount of coagulant dose. Maximum percentage removal comes 99.84% in case of 15 mg coagulant dose at the time interval of 90 min. Percentage removal is effective up to one hour so ,on after that adsorption surfaces virtually get saturated and adsorption are decline.

5.4 Comparison of efficiency of coagulants

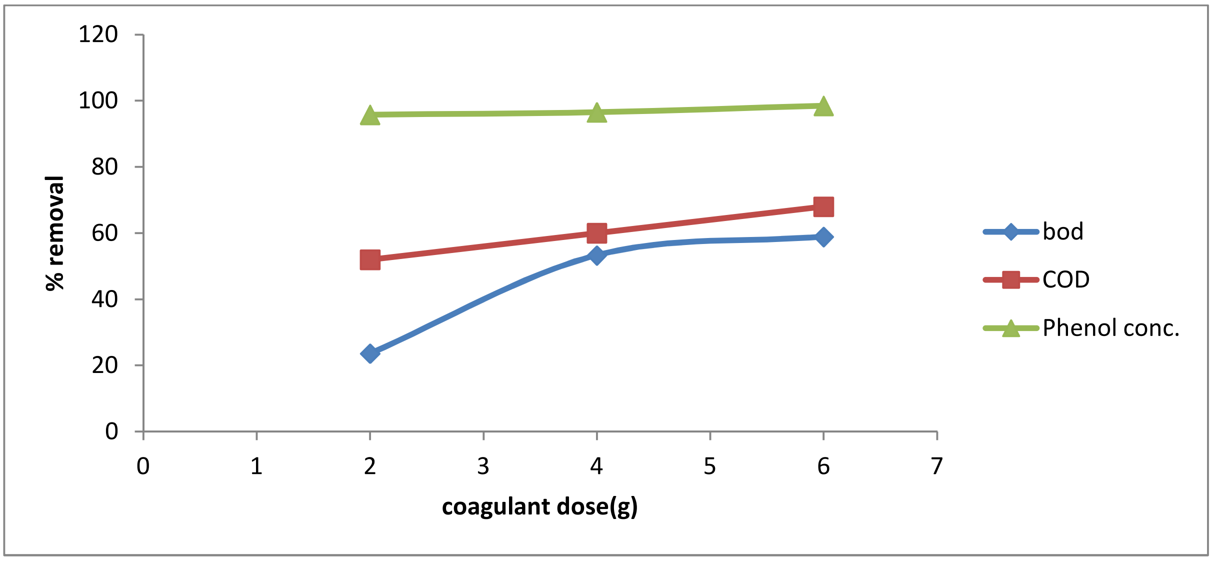
a) Comparison of BOD, COD & phenol conc. after coagulation.



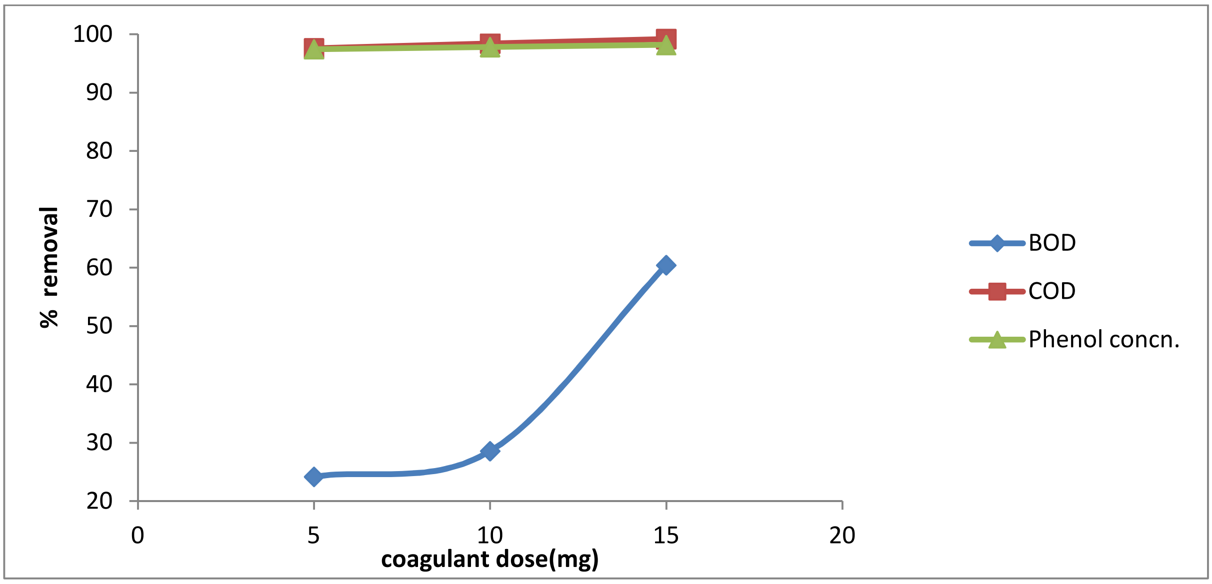
Amount of coagulant used in coagulation with Ferric Chloride is less than the amount of coagulant used with Aluminium sulphate. Despite of using very less amount, percentage removal of BOD, COD, and phenol concentration is more in Ferric Chloride which is 59.89 %, 68 %, 98.51 % ,respectively. Whereas value of BOD, COD, and phenol concentration is 43.4 %, 52 %, and 96% respectively in case of Aluminium Sulphate as a coagulant. Study shows Ferric Chloride is better coagulant than Aluminium Sulphate.



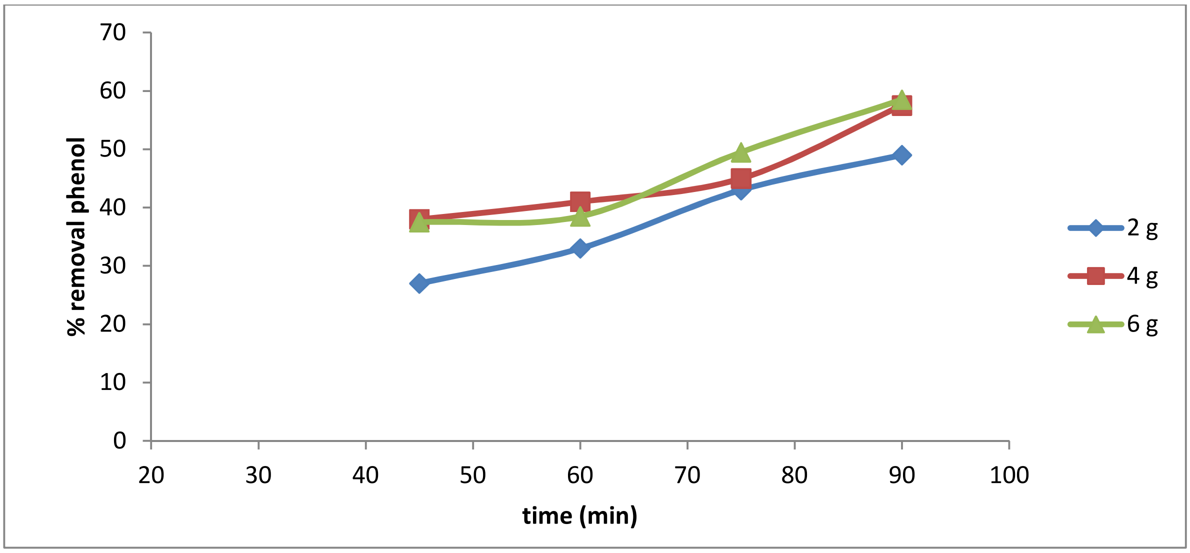
b) comparison of BOD,COD & phenol conc. after adsorption of supernatant collected after coagulation



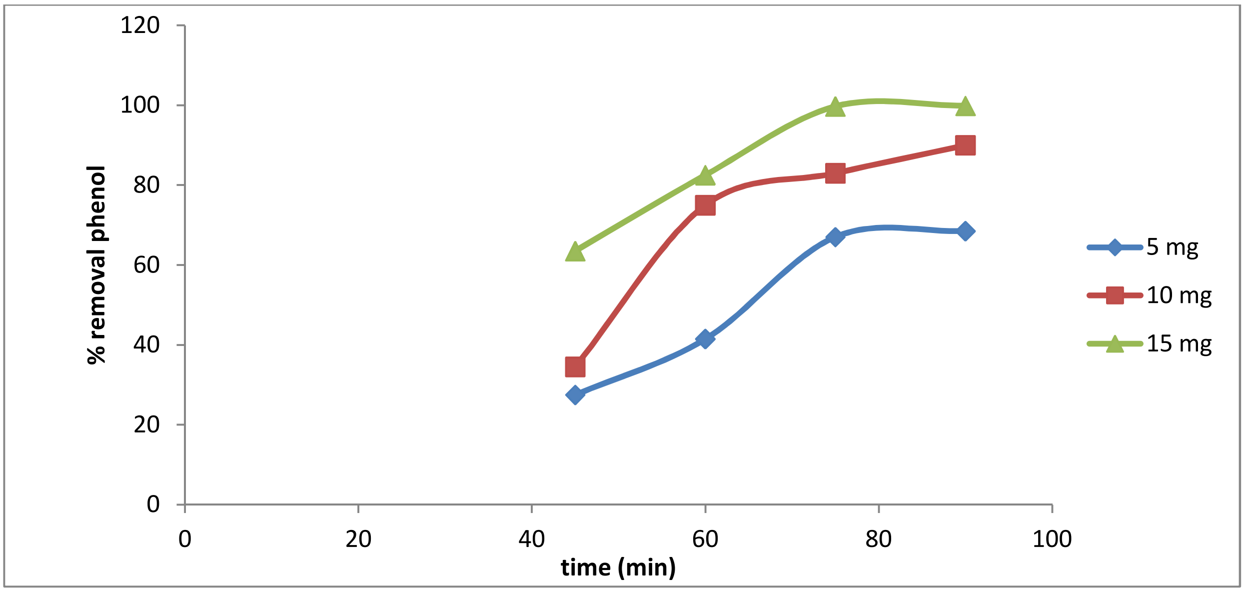
Despite of using less amount of Ferric Chloride in comparison of Aluminium Sulphate, percentage removal of BOD, COD, and phenol concentration is more in Ferric Chloride which is 60.43 %, 99.2 %, 98.18 % ,respectively. Whereas value of BOD, COD, and phenol concentration is 59.89 %, 60 %, and 97.81% respectively in case of Aluminium Sulphate as a coagulant.



c)comparison of phenol percentage removal after adsorption of supernatant with fly ash



Despite of using very less amount, percentage removal of phenol is more in Ferric Chloride with respect to Aluminium Sulphate. Percentage removal of phenol in Ferric Chloride is 99.84% whereas 58.5 % in Aluminium Sulphate. In case of Aluminium Sulphate maximum phenol removal in 6 g of coagulant dose, and in Ferric Chloride 15 mg of coagulant dose show maximum removal, which is very low in comparison of amount of Aluminium Sulphate.



5.5 Isotherm, kinetics and Thermodynamics study

Thermodynamics, kinetics and Isotherm study have been done of adsorption process. Adsorption has been done of the supernatant after the coagulation of phenolic waste water with Aluminium Sulphate and Ferric Chloride .Thermodynamics, Kinetics and Isotherm studies are shown below in graph form.

5.5.1 Isotherm study

a)

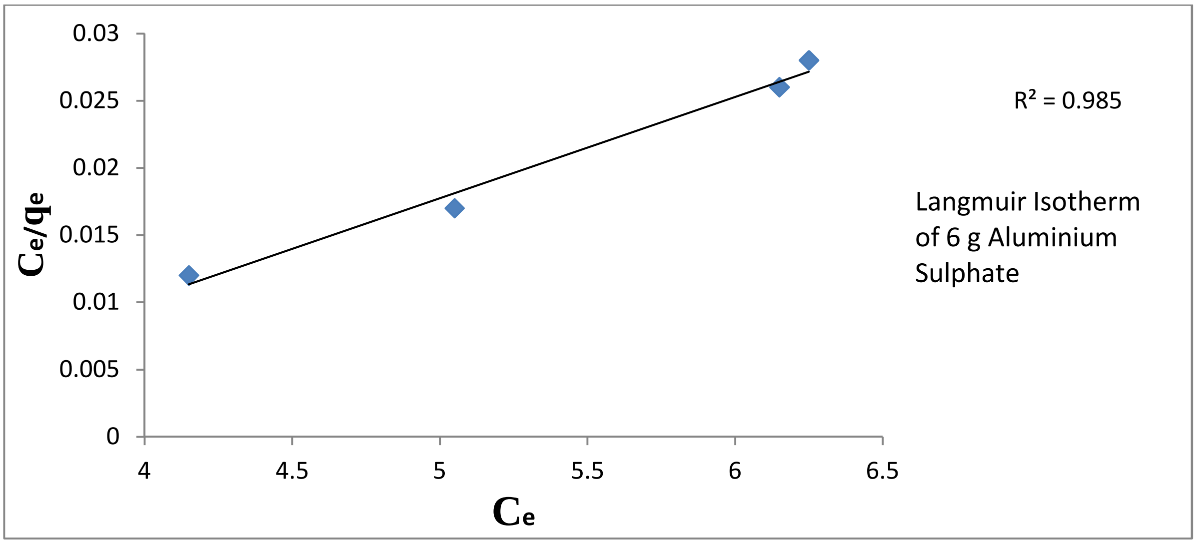


Fig 15: Plot of C_e/q_e vs C_e

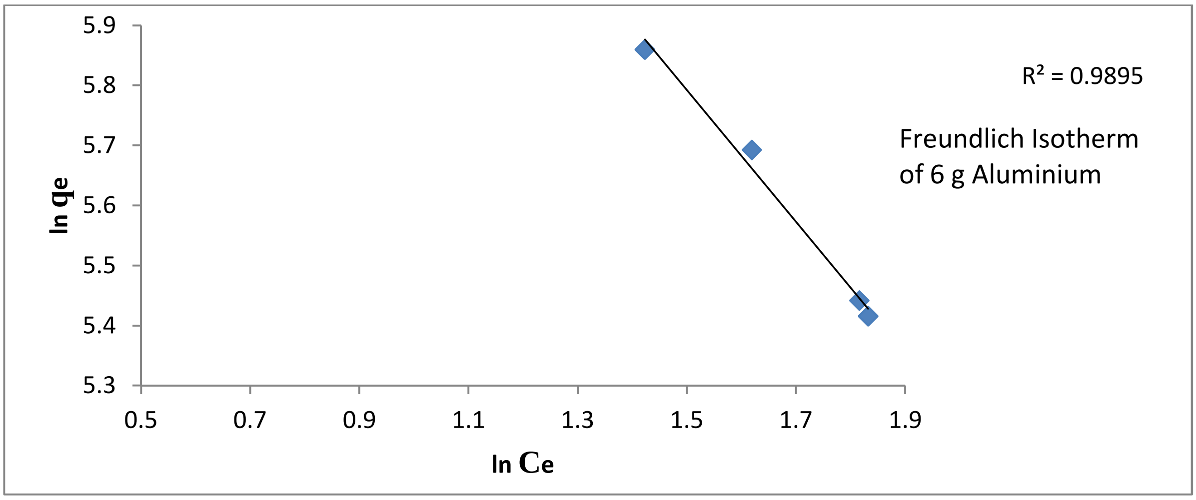


Fig 16: Plot of ln q_e vs ln C_e

Both plot gives straight line but value of R^2= 0.9895 in Freundlich Isotherm is more than the value of R^2= 0.985 in Langmuir Isotherm means that the above adsorption will follows **Freundlich Isotherm**. From this we can say that multilayer adsorption is taking place.

b)

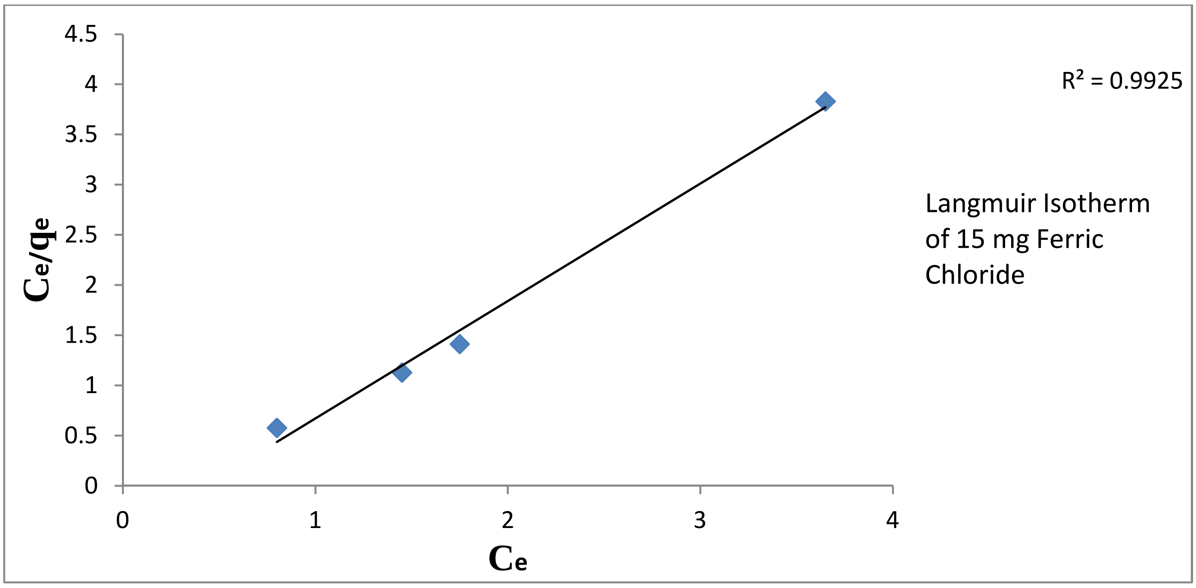


Fig 17: Plot of C_e/q_e vs C_e

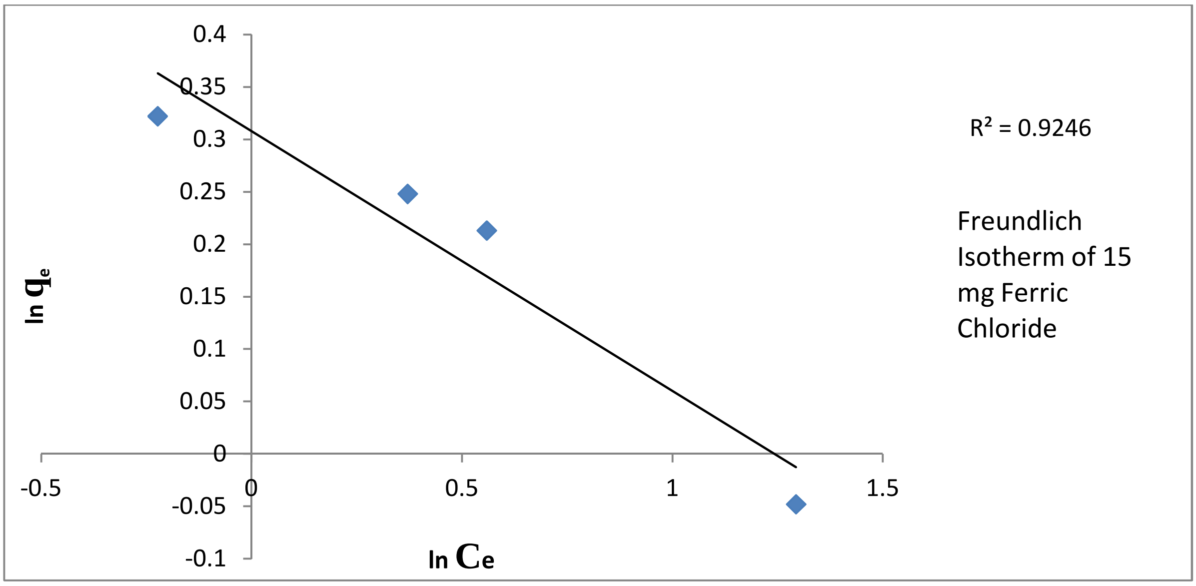


Fig 18: Plot of ln q_e vs ln C_e

Both plot gives straight line but value of R^2= 0.9925 in Langmuir Isotherm is more than the value of R^2= 0.9246 in Freundlich Isotherm means that the above adsorption will follows **Langmuir Isotherm**. From this we can say that

- ✓ Monolayer adsorption occurs.
- ✓ Molecules are adsorbed at discrete active sites on the surface.
- ✓ Each active sites adsorbing one molecule only.
- ✓ The adsorbing surface is energetically uniform.
- ✓ And no interaction between adsorbed molecules occurs.

As the adsorption follows Langmuir Isotherm there is 80% chances of being physical adsorption.

5.5.2 Kinetic study

a)

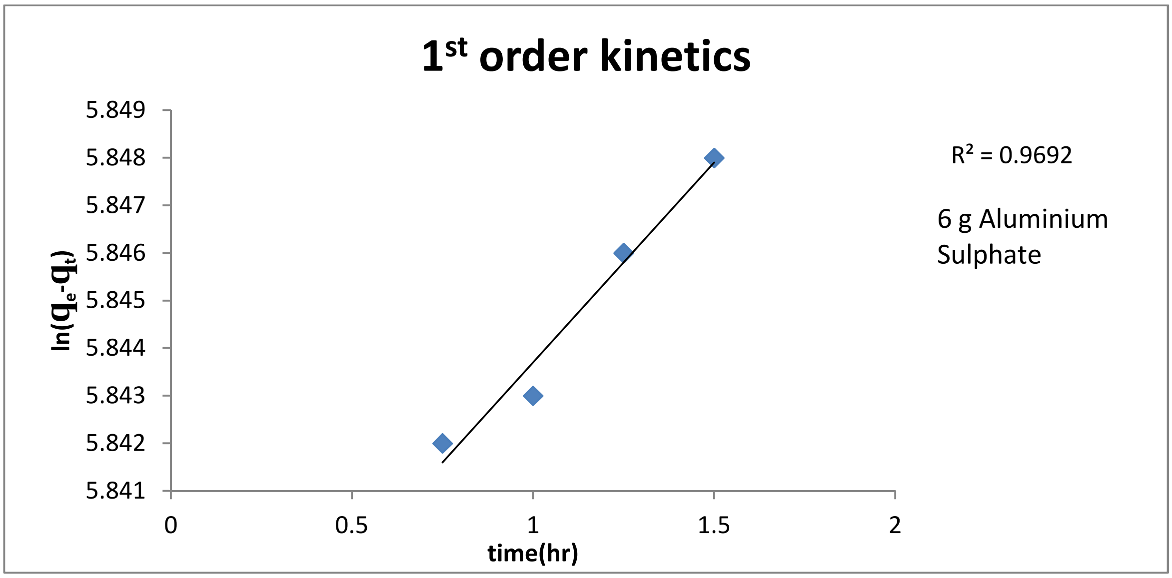


Fig 19: Plot of $\ln(q_e\text{-}q_t)$ vs time (hr)

From the plot of 1st order and 2nd order kinetics we can see that value of R^2= 0.9692 comes more in 1st order kinetics in comparison of 2nd order kinetics, means that the plot will follow **1st order kinetics**.

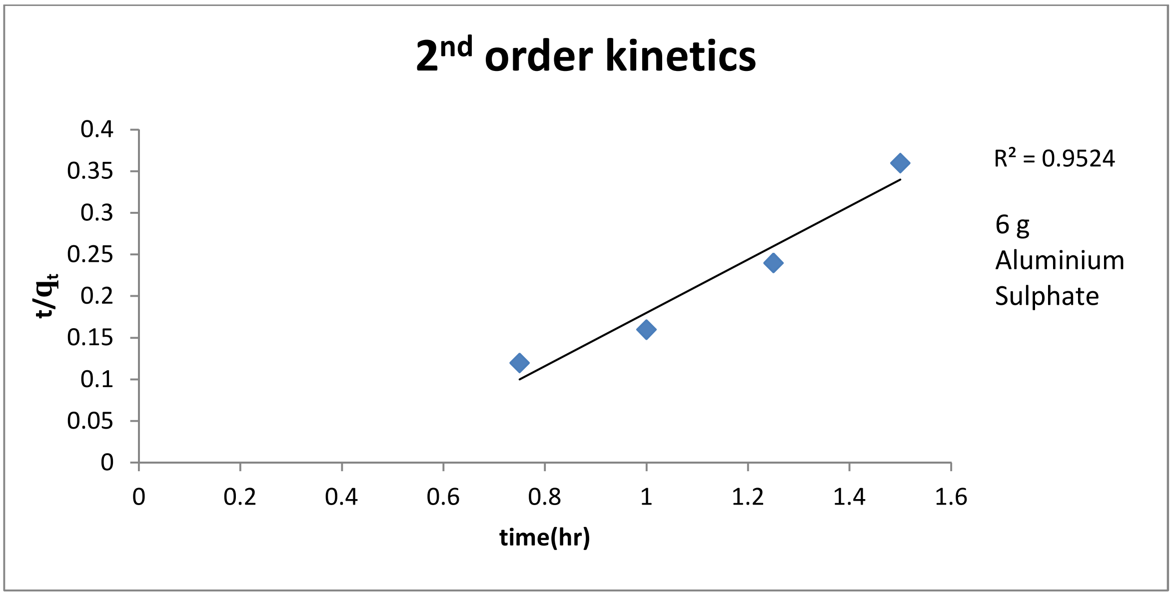


Fig 20: Plot of t/q_t vs time (hr)

b)

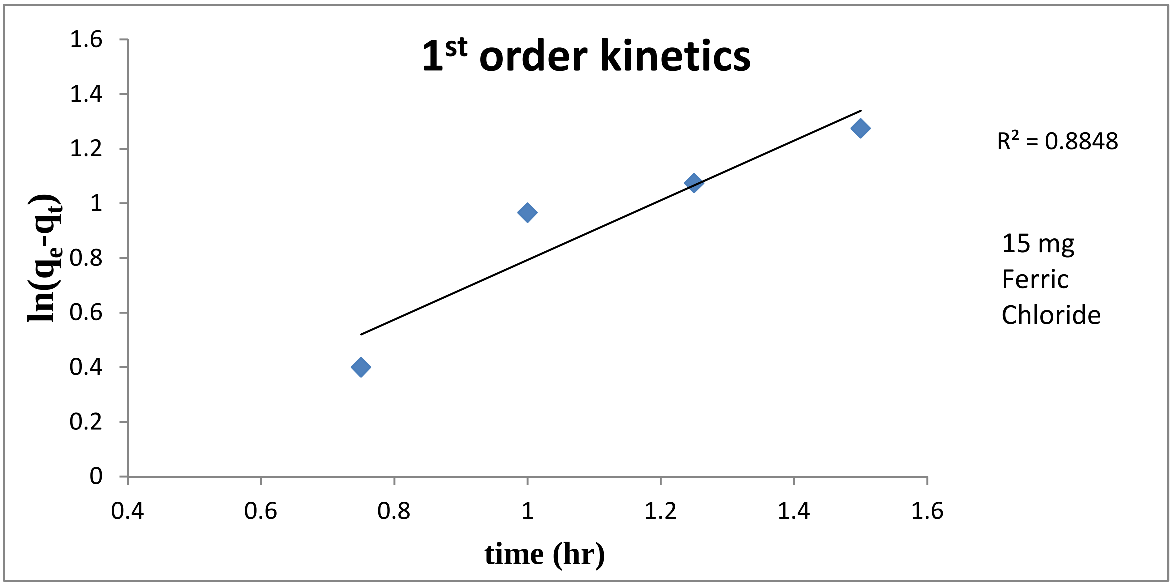


Fig 21: Plot of ln(q_e-q_t) vs time (hr)

From the plot of 1st order and 2nd order kinetics we can see that value of R^2= 0.9746 comes more in 2nd order kinetics in comparison of 1st order kinetics, means that the plot will follow **2nd order kinetics**.

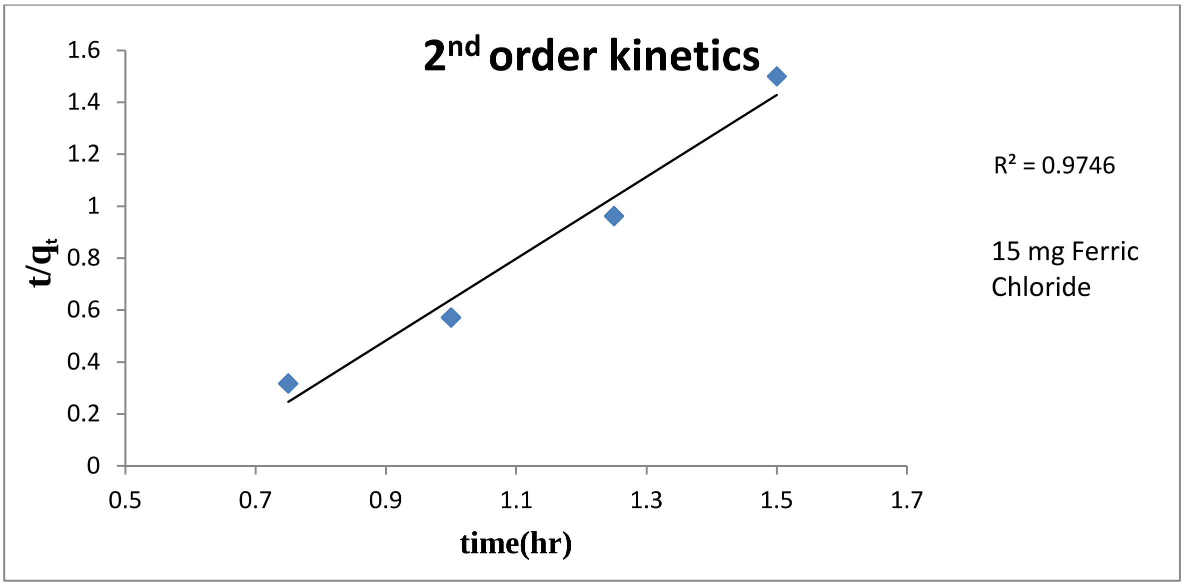


Fig 22: Plot of t/q_t vs time (hr)

5.5.3 Thermodynamics Study

a) Activation energy parameters

The activation energy is the minimum kinetic energy required for a particular reaction to carry out.

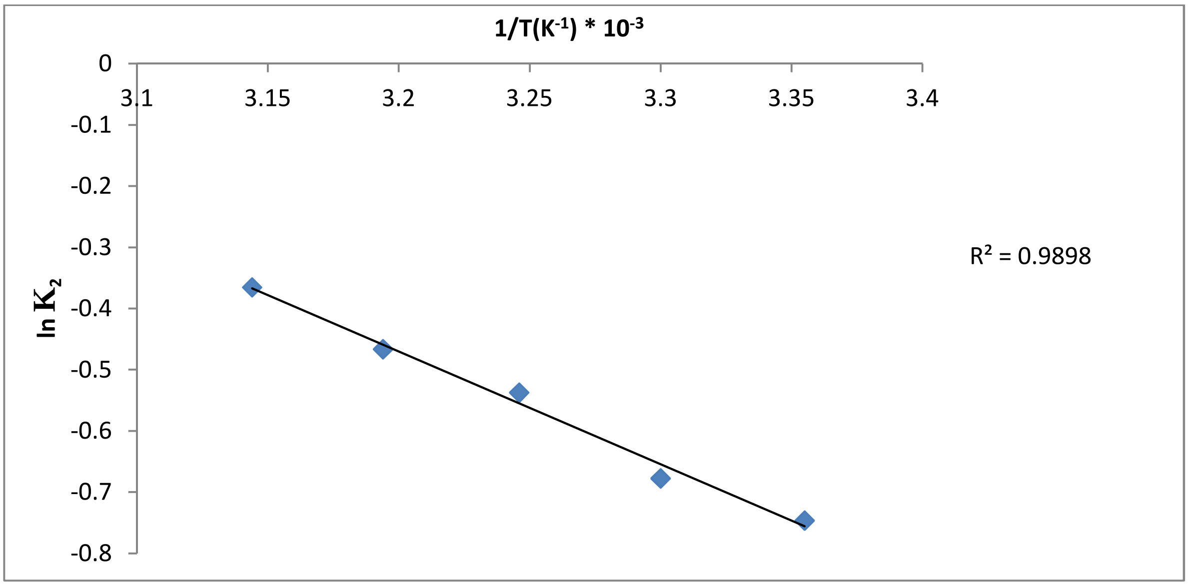


Fig 23: Plot of ln k_2 vs. 1/T.

The relationship between the rate constant and temperature can be described by the linear form of the Arrhenius equation that expressed by the following equation:

$$\ln k_2 = \ln A - Ea/RT$$

Where Ea is the activation energy, J/mol, A is the Arrhenius constant, g/mg min, k_2 is the pseudo-second-order rate adsorption constant, g/mg min ,R is the ideal gas constant, 8.314 J/mol K, and T is the solution temperature, K. The magnitude of activation energy may give an idea about the type of adsorption. To calculate the activation energy (E_a) for the adsorption process, ln k_2 is plotted versus 1/T as shown in above figure. The value of activation energy (E_a) for the adsorption is calculated to be approximately **15.3185 J/mol**. These values indicate that **physical adsorption** mechanisms occurred because value is less than 40 J/mol.

b) Thermodynamic parameters

Determination of thermodynamic parameters has a great importance to evaluate the spontaneity and the heat change of the adsorption processes. The experimental data obtained at different temperatures are used in calculating the thermodynamic parameters. Based on fundamental thermodynamic concepts, it is assumed that in an isolated system, energy cannot be gained or lost and the entropy change is the only driving force. The thermodynamic parameters are; the changes in the standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), due to the transport of unit mole of solute from the solution on to the solid–liquid interface. The relationship between the adsorption equilibrium constant and temperature can be expressed by Van’t Hoff equation

$$\ln K_2 = -\Delta G^o / RT = \Delta S^o / R - \Delta H^o / RT$$

Where R is the universal gas constant, 8.314 J/mol K, T is the absolute solution temperature, K, and K_2 is adsorption equilibrium constant, l/mg. ΔH^o, ΔS^o, and ΔG^o are the change in enthalpy, entropy and free energy, respectively. The slope and the intercept of the plots of ln K_2 versus 1/T are used to determine the ΔH^o and ΔS^o values. ΔG^o can be calculated by the following formula

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

So, from the above plot we obtained $\Delta S^o = 5.426$ J/mol K

$\Delta H^o = -1.8245$ J/mol

And, ΔG^o (298 K) = -1618.79 J/mol

ΔS^o has a positive value which means **increasing randomness** at the solid/liquid interface.

The negative values of ΔH^o are indicating that the adsorption reaction is **exothermic**.

The negative values of ΔG^o indicates that the adsorption process has a **spontaneous** nature, spontaneous nature of reaction suggest that no external energy is required to complete the process.

Conclusion

This present research work has demonstrated the potential of using $FeCl_3$ and fly ash as a promising, efficient, economic, available, and environmentally friendly coagulant and adsorbent respectively for a very hazardous phenol removal from industrial waste water. Coagulation followed by adsorption would be useful and efficient treatment of waste water containing phenol. Based on the experimental results of this study, the following points can be concluded.

1)The optimum operating conditions for phenol adsorption is by using(100 mg fly ash for 10 ppm phenol concentration, pH= 4 at 45^{o}c for 90 min with 150 rpm shaking speed).

2) Coagulant $FeCl_3$ have shown better result in destabilization of colloidal particles in phenolic waste water, than other coagulant like $Al_2(SO_4)_3$.

3) Despite of using less amount of $FeCl_3$ (15 mg) ,percentage removal of BOD, COD, and phenol concentration was more in this coagulant which were 59.89%, 60%, 98.51 %, respectively. Whereas percentage removal of BOD, COD, & phenol concentration were 43.4 %, 52%, & 96 % respectively in case of $Al_2(SO_4)_3$ (6 g) as a coagulant.

4) After adsorption on fly ash percentage removal of BOD, COD, & phenol concentration were also more in case of $FeCl_3$ with respect to $Al_2(SO_4)_3$.

5) In case of $FeCl_3$ BOD, COD, & phenol concentration was 60.43 %, 99.2%, & 98.18% , whereas in case of $Al_2(SO_4)_3$ values were 59.89%, 60%, and 97.81% respectively.

6) On optimum condition of adsorption percentage removal was 99.84 % (after coagulation with $FeCl_3$) whereas after coagulation with $Al_2(SO_4)_3$ percentage removal was only 58.5 %.

7) Isotherm, kinetics, and thermodynamics study have been done to describe the adsorption process mechanism.

8) After coagulation with $Al_2(SO_4)_3$,adsorption process follows Freundlich isotherm means that multilayer adsorption taking place and after coagulation with $FeCl_3$,adsorption process follows Langmuir isotherm means that monolayer adsorption taking place.

9) After coagulation with $Al_2(SO_4)_3$,adsorption process follows 1st order kinetics ,whereas after coagulation with $FeCl_3$, adsorption process follows 2nd order kinetics, pointing that the adsorption mechanism is physical adsorption process.

10) Study of thermodynamics parameters indicates that adsorption process on fly ash is spontaneous and exothermic.

Due to the fly ash low cost, technical and economical feasibility, abundant availability, environmental benefits, high adsorption capacity , user friendly and eco-friendly ,it can be utilized as a promising adsorbent for phenol removal in the future for efficient large scale phenol removal from waste water. Also coagulation followed by adsorption process showed increased efficiency of phenol removal.

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