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Review On Studies Of Different Methods For The Removal Of Phenol From Waste Water

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***Abstract:** Since times immemorial, there has been an intricate ecological balance and one of the biggest problems of modern world is environmental pollution, which threatens this very balance that supports life on Earth. Industrial waste often includes carcinogenic substances like phenols, synthetic dyes that are non-degradable and toxic. Phenolic compounds are found in wastewaters of various industries such as petroleum refining, coal conversion, plastics, textiles, iron and steel manufacturing as well as pulp and paper manufacturing. Phenols are extremely toxic to humans, plants and other animals. It is very important to remove phenols and aromatic compounds from contaminated water before discharge into any natural water because of their toxicity to aquatic organisms. This paper takes a look at the different methods like physical, chemical and biological used for the removal of phenol. The method applied for any particulars removal process depend upon the feasibility and requirement.*

***Keywords:** Phenol, Wastewater, Pervaporation, Extraction, Biological methods, Adsorption, Photodecomposition*

I. INTRODUCTION

Phenols are important industrial chemicals of environmental concern since they are involved in many industries such as coke, refineries, manufacture of resin, pharmaceuticals, and pesticides. Presences of phenolic compounds even at low concentration in industrial waste adversely affect aquatic as well as human life directly or indirectly. Phenolic compounds are present in the environment as a result of their uses and the processes in which they are implicated. Although they can be originated naturally due to the degradation of humic substances, tannins and lignins. High concentrations of phenol and phenolic compounds typically are found in aqueous effluents of oil refineries, petrochemical, ceramic, textiles, dyes, pesticides, paper, steel plants, coal conversion processes, phenolic resin and pharmaceutical industries. (Sachin B. Divate, Rahul V.Hinge, 2014). Phenols are toxic and potentially carcinogenic and can affect the taste and odour of drinking water with concentrations as low as a few μgL^{-1}. They are known as noxious pollutants.

A number of effects from breathing phenol in air have been reported in humans. Short-term effects reported include respiratory irritation, headaches, and burning eyes. Chronic effects of high exposures include weakness, muscle pain, anorexia, weight loss, and fatigue. Effects of long-term low-level exposures include increases in respiratory cancer, heart disease, and effects on the immune system (Susmita M and Jayanta B, 2007). Repeated exposure to low levels of phenol in drinking water has been associated with diarrhea and mouth sores in humans. Ingestion of very high concentrations of phenol has resulted in death. In animals, drinking water with extremely high concentrations of phenol has caused muscle tremors and loss of coordination (Kavitha D and Namasivayam C, 2007). As a consequence, both, the US Environmental Protection Agency (EPA) and the European Union (EU) have included some phenols, mainly chlorophenols and nitrophenols, in their lists of priority pollutants. EU Directive 2455/2001/EC sets a maximum concentration of 0.5 μgL^{-1} in drinking water and their individual concentration should not exceed 0.1 μgL^{-1}. However, World health organization's (WHO) Guidelines for drinking water quality gives the level of phenols as 0.001 mg/L. (Kumaran and Paruchuri, 1997); (Nuhoglu and Yalcin, 2005) and (Saravanan et al., 2008).

Industries	Type of Phenols
Textile	Phenol, Chloro phenol, Alkyl phenols, Catechol, Chloro catechol, Nitro phenol.
Wood processing	Phenol, Chloro phenol, Alkyl phenols.
Pharmaceutical	Catechol, Chloro cetachol, Chloro phenol, Methyl phenol, Buthyl hydroxyl toluene,Buthyl droxyanisole.
Rubber	Aminophenol, Cetachol, Chlorocetachol, Amino phenols, Buthyl hydroxyl toluene, Buthyl hydroxyanisole
Petrochemical	Phenol,Methyl phenol
Cosmetics	Chlorocetachols, Methyl phenol, Buthyl hydroxyl toluene, Buthyl hydroxyanisole
Coal-tar production	Phenol, Nitrophenols, Methyl phenols.

Table 1: Various industries and its associated phenols. (W.Duda et al (2007)

A wide variety of methods are employed for removal of phenol like, Liquid-Liquid Extraction, Pervaporation, Adsorption, Enzymatic Degradation, Microbial Degradation etc. Most of these methods belong to physical, chemical and biological methods.

II. VARIOUS METHODS FOR PHENOL REMOVAL

PHYSICAL METHODS

LIQUID-LIQUID EXTRACTION: Process in which components of a solution are separated based on their relative solubilities. It is a very simple method for removal of phenols using solvents (Paivab. J.L. Palmaa M.S.A and Zilli M, 2007) worked on the batch removal of phenol by liquid-liquid extraction from methyl isobutyl ketone (14.4%) as solvent, in a bench-scale mixed vessel. Parameters that influence phenol removal like temperature, concentration of NaOH in the extracting aqueous phase and rotational speed were analysed. The temperature range was 10 ^{O}C to 40 ^{O}C, along with NaOH concentration between 5.5 and 6.5% and the range of rotational speed was between 400 to 800 rpm. The removal efficiency was noted to be 94.0-97.6%.

THREE PHASE LIQUID SYSTEM: Three phase liquid system is composed of organic extractant, high molecular polymer and salt. (Pinhua Yu, Zhidong Chang, Yinchen Ma, Senjian Wang, Hongbin Cao, Chao Hua, Huizhou Liu, 2009) investigated separation of P-Nitro phenol and O-Nitro phenol by using a three phase extraction system. About 85% of O-Nitro phenol and 90% of P- Nitro phenol was recovered using this method at pH 4.

PERVAPORATION: Pervaporation is a separation process wherein the compounds are separated from the solution by partial vaporisation through a non-porous or porous membrane. The two steps involved in this process are permeation and evaporation. The membrane used acts as a selective barrier that allows the desired component of the liquid feed to pass through it by vaporisation. (Wojciech Kujawski, Andrzej Warszawski, Włodzimierz Ratajczak, Tadeusz Por¸ebski, Wiesław Capała, Izabela Ostrowska, 2004). Worked on Pervaporation and adsorption for phenol removal. Various membranes like PEBA, PERVAP1060 and PERVAP1070 were used. All the membranes were found to be selective for phenols. PEBA membrane showed the highest selectivity for phenol removal but, they are not commercially available, PERVAP1060 and PERVAP1070 membranes are commonly used.

NANO FILTRATION: Nano-filtration is a membrane filtration process. Membrane pore size ranges from 1-10 nanometers. Nano filtration can be used either for water softening or for removal of disinfectants from water (Bódalo A et al 2009) used different nano filtration membranes like, NF-97, NF-99, DSS-HR98PP for the reduction of phenol concentration under different experimental conditions. DSS-HR98PP membrane showed the highest efficiency.

ADSORPTION: It is a surface phenomenon. A film of adsorbate is formed on the surface of the adsorbent. Surface energy is the consequence of the adsorption process. Adsorption process can be classified as physisorption (van der waals forces) and chemisorption (covalent bonding) depending on the forces between adsorbate and adsorbent. Adsorption is generally described through isotherms where the amount of adsorbate formed on adsorbent is the function of pressure (if gas) or concentration (if liquid), at constant temperature. Various isotherm models are present till date such as Henry adsorption constant, Freundlich constant, Langmuir, BET theory, adsorption enthalpy and so on. Adsorption is one of the most probed techniques for removal of Phenol from industrial waste water. The research in this particular field has been very vast. Different agricultural, microbial, chemical and synthetic sources are listed in Table 5 and synthetic sorbents in Table 4. They have been tested for their adsorption capacities of organic pollutants, including phenols. Due to diverse sources, adsorption can be performed in fluidised bed reactor, fixed bed reactor, trickle bed reactors and many more. Owing to its versatility and ease of operation, it is one of the most commonly used waste water treatment methods for removal of phenols and phenolic compounds.

CLOUD POINT EXTRACTION METHOD: It is an advanced physical method for phenol extraction from waste water. Most of the non-ionic surfactants form micelles in aqueous solutions and they get separated into two phases, when heated above a particular temperature, known as the cloud point temperature. A micelle is an aggregate of molecules formed within a liquid colloid. The hydrophilic part of the micelle is subjected towards the surrounding solvent and the hydrophobic part towards the micelle centre. This method is largely dependent on the non-ionic surfactant used for phenol separation and consequent degradation. Usually the extraction efficiency increases with increase in concentration of surfactants. (Raiti J. et al 2014) investigated the two phase extraction of phenolic compounds from pre-treated olive mill waste water using aqueous. Micellar formation. Triton X-114 was used as the surfactant, and in this case, the phenol recovery higher than 60% was achieved. Different variables like surfactant concentration, pH and equilibration temperature were tested. Studies done by (Dr. Sirshendu De 2013), when two non-ionic surfactants TX-114 and TX-100 were employed for removal of a 100 ppm dye, it was observed that for surfactant concentration of 0.25 (M) more than 95% of dye was removed. Therefore, the dye extraction was almost 95% for TX-100 and 100% for TX-114.

CHEMICAL METHODS

THREE PHASE ELECTRODE SYSTEM: The three phase electrode system is an advanced method to remove phenol from waste water. (Ya Xiong et al 2003) worked on the performance of three-phase three-dimensional electrode reactor for the reduction of COD in wastewater-containing phenol and it was compared with granulated activated carbon (GAC) adsorption bed and 3d electrode system. COD removed was 1350ppm at 200th batch run, with airflow of 5 l min¯1, cell voltage of 30V for 30 min and 1000ppm, 610ppm from three phase three dimensional electrode, GAC and 3D electrode system respectively. Hence, three phase three dimensional electrode system was found to be much efficient for the removal of COD in phenol containing waste water.

ELECTROCOAGULATION: In this method, phenol is removed by electrocoagulation in which the sacrificed anodes form active coagulant that is then used to remove pollutant by precipitation and flotation in situ. Electrochemical cells containing an electrode arrangement in contact with polluted water are employed during electrocoagulation. (Ashtoukhy et al 2013) worked on removal of phenolic compounds by electrocoagulation from petrochemical waste water using a fixed bed reactor. The conclusion was that with increase in current density from 1.2 to 9.82 mA/cm2, there was a significant increase in the percentage removal of phenol from 40% to 88%. Several parameters like the effect of NaCl, temperature, pH and initial phenol concentration were tested for optimum conditions to facilitate phenol removal. At high current densities, pH 7 and time duration of 2 hours, 97% phenol removal was attained.

PHOTODECOMPOSITION: (Iliz et al 2003) worked on photodecomposition of phenol irradiated with near UV radiation in the presence of aqueous TiO_2 suspensions. This heterogeneous degradation of phenol followed zero-order kinetics and up to 70% conversion was seen. In the presence of Silver ions, the results indicated the phenol can get degraded via direct electron transfer. (Raquel Cruz et al 2011) investigated the photo catalytic degradation of phenolic compounds from the effluent of dye industry. In the presence of aqueous TiO_2, up to 99% phenol was removed after 4 hours at pH 5. Under the same conditions the percentage removal of other phenolic compounds was 92% for 2 Chloro phenol and 83% for 2,4dimethyl phenol.

BIOLOGICAL METHODS

Biodegradation of phenols is the process of breakdown of the phenol into a simpler/non-toxic compound by the action of microbes or enzymes. The two main types of biological degradation of phenols are enzymatic degradation and microbial degradation.

ENZYMATIC DEGRADATION: The enzymes, obtained from various sources are popularly being used for wastewater treatment. Among the many enzymes, polyphenol oxidases and peroxidases are widely used.

According to (Nagai and Suzuki 2001), polyphenol oxidase is a copper-containing enzyme and the classification of PPO is as follows:

TYROSINASE: Tyrosinase, also called catecholase, contains a binuclear copper containing active site that facilitates the degradation reaction of the phenols. It catalyzes the hydroxylation of mono-phenols to o-bi phenols, which is then degraded to form o-quinone by dehydrogenation reaction. The use of the Tyrosinase enzyme can be coupled with various other techniques like integration into a biosensor, adsorption or immobilization techniques for better results

LACCASES: Laccases are the enzymes that catalyze the degradation reaction by reduction of oxygen to water along with oxygenation of a phenolic molecule. They are also called large blue copper proteins or blue copper oxidases. They contain four neighboring copper atoms at different binding sites, where two are involved in electron capture and transfer, and two other with the binding of oxygen. On oxidation, the phenols are converted to o-bi phenols which may undergo further enzymatic degradation or may undergo polymerization reaction leading to formation of melanin-like dark brown accumulated product.

(Ulfat Jan et al 2000) worked on Detoxification of Phenols and Aromatic Amines from waste water by Using Polyphenol Oxidases. Sources of polyphenol oxidase: Gooseberry, quince leaves, tea leaves, banana fruit/ peel, potato etc.

(Jadhav et al 2011) isolated and characterized the polyphenol oxidase (PPO) enzyme from banana peel. The PPO enzyme was used to treat industrial waste water containing phenol. The enzyme activity, optimum pH, optimum temperature, phenol degradation and phytotoxicity studies were conducted. Complete degradation of phenols was seen in 24 hours for smaller concentration of phenols, and 72 hours for higher phenol concentrations. The optimum temperature and pH for maximum enzyme activity was seen to be 35̊ C and 7 respectively.

Peroxidases, are found in various plants and microbes. Sources of peroxidase: Raddish, cabbage, tobacco etc. The different types of peroxidase enzymes are manganese peroxidase, lignin peroxidase, horse raddish peroxidase, etc.

MICROBIAL DEGRADATION: (Paula M. van Schie et al 2000) describe the use of micro-organisms in biodegradation of Phenol. The degradation of phenol by this method is more useful due to its ease of manipulation of strains and scaling up of the process. The phenol is converted to catechol by oxygenation, which is further broken down and the compounds enter the TCA\other metabolic cycle in order to produce carbon dioxide, water or other inorganic simple compounds. The degradation can be either aerobic and anaerobic conditions. Aerobic Degradation: In aerobic degradation, the phenol is oxidized to catechol by the microbial enzyme phenol hydrolase in the presence of NADH2. Depending on the enzymes in the organism used, it is degraded into either cis muconic acid or 2- hydroxymuconic semi-aldehyde, which may enter the Krebs cycle and get degraded to carbon-dioxide and water. The various organisms involved in aerobic degradation are Acinetobacter calcoaceticus, several organisms from Pseudomonas species, a thermophilic Bacillus species, Streptomyces setonii, and two eukaryotic microorganisms: the yeasts Trichosporon cutaneum and Candida tropicalis.

ANAEROBIC DEGRADATION: The degradation of phenols may occur in the absence of oxygen. Anaerobic degradation usually occurs in the methanogenic, nitrate reducing, sulphate reducing or iron reducing conditions. The mechanism however, varies from one organism to another. In a nitrogen reducing bacteria called Thauera aromatic, the phenol ring is carboxylated at its para-position to 4-hydroxybenzoate which is further degraded.The organisms involved in anaerobic degradation are Thauera aromatica strain K172, Geobacter metallireducens (iron- reducing conditions), the sulfate reducing organism Desulfobacterium phenolicum, Desulfotomaculumsp. strain Groll (in presence of bi-carbonate) and Desulfovibrio species. (S.E Agarry et al 2008) worked on strains of Pseudomonas fluorescence at different concentrations of phenol. A comparative study of the performance of Pseudomonas fluorescence and other micro-organisms was carried out. Complete degradation of phenol was seen by the action of the bacteria. The increase in the concentration of phenols led to an increase in degradation time from 84-354 hours.

III. CONCLUSION

There has been extensive research in the field of phenol removal from industrial waste water corresponding to finding a suitable method with higher phenol removal efficiency, ease of operation, feasibility and easy scale up to the industrial level. Several physical, chemical and biological methods have paved way for newer innovative techniques that could be employed in the waste water treatment. Based on ease of operation, scalability, economic feasibility and variety of other factors like phenol recovery, downstream processing, conditions to be maintained, it can be concluded that Biological method for phenol detoxification is most preferred.

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