ABSTRACT

Aqueous phenolic wastewaters are relatively common industrial effluents, being produced in several processes viz. coking, petroleum refinery, pharmaceuticals, dyes, pesticides, etc. Stringent regulations prescribed by regulatory authorities and toxic effect of phenols on ecology have led researchers to explore the technology, which is ecologically and economically feasible for phenolic waste treatment. Various treatment technologies available in the literature are reviewed and summarized in Chapter 1 Table 1.2. From the various technologies available three have been selected for the present work, because they seem to be of industrial importance. The technologies selected are: **adsorption, biosorption and advanced oxidation processes**.

In adsorption, use of fly ash as an adsorbent, a waste material obtained from four different industrial sources, has been explored. Use of fly ash for removal of phenol serves dual advantage of waste management. Literature review envisages the use of fly ash as an adsorbent for phenol removal; however, phenol removal depends on source, composition and other inherent characteristics of fly ash. No work has been reported on the adsorption of phenols on fly ash obtained from different sources. In the present work, fly ash obtained from following sources have been investigated: Lignite based fly ash A from Gujarat Industrial Power Corporation Ltd., Surat, Coal based fly ash B from Gujarat Electricity Board, Ukai, Coal based fly ash C from J.K. Paper Mill, Songadh and Bagasse based fly ash D from Sayan Sugar Industries, Surat. Also, most of the studies published in literature are on phenol, nitrophenol, cresol, and chlorophenol. In the present work adsorption studies on phenol, catechol, resorcinol, hydroquinone, 2-aminophenol, and 3-aminophenol using fly ash were carried out. The effect of various parameters (pH, temperature, initial concentration, mass of adsorbent, presence of salt and contact time), isotherms, thermodynamics and kinetic studies of different phenolic compounds on fly ash from different sources were studied in batch reactor. All these studies were repeated using activated carbon as adsorbent for comparison. The results obtained are presented in Chapter 3. Decrease in temperature (60 to 30°C) has been found to increase the adsorption of all the phenols. Whereas decrease in pH has been found to increase the adsorption of hydroxy phenols. Lower pH (2.0) and higher pH (11.0) have been found to be favorable for aminophenol adsorption on fly ash B, C and D. Incase of fly ash A, low pH(2.0) whereas in case of activated carbon high pH(11.0) has been found to be favorable for adsorption of aminophenols. The percent removal of phenols was found to increase with the decrease in initial concentration (500 to 25 mg/l), however, the uptake of the compounds on the adsorbent decreases with the decreasing initial concentrations. All the phenols showed the similar adsorption behavior. Addition of 1 M NaCl or 0.5 M Na_2SO_4 increases sorption rate and also increases the percentage removal by 1 to 3 %. The increase in amount of adsorbent increases

the percentage removal and decreases the adsorption density. The optimum amount of adsorbent for the adsorption of phenols on; fly ash A 2.5, fly ash B 2.5, fly ash C 2.5, fly ash D 1.5 and activated carbon 0.5 g in 100 ml was found respectively. The relative adsorption capacity of phenolic compounds for different adsorbents is:

activated carbon > fly ash D > fly ash B> fly ash A> fly ash C

The difference in adsorption capacity of these adsorbent can be explained on the basis of surface area and carbon content of different adsorbents. Negative values of enthalpy obtained by thermodynamic analysis reveal that adsorption is exothermic process in all the cases studied.

Lagergren's pseudo first order kinetics and pseudo second order kinetics given by Ho and Mckay have been employed for kinetic studies. Pseudo second order kinetics was better fit with correlation coefficient more than 0.99 than first order kinetics. Second order rate constant was found to decrease with increase in concentration. For sorption rate, no definite conclusion could be drawn. Further analysis of the kinetic data for determining the rate controlling step using Weber-Morris plot indicate that the rate of adsorption was film and intra-particle diffusion controlled. From these plots, it may be concluded that there are three regions of change of rate of adsorption: rapid, medium, and slow. The values of effective diffusion coefficient calculated using Vermeulen and Urano approximations were found to be in the range of 10^{-12} to 10^{-14} m^2/s for all the phenols on all the types of fly ash. However for activated carbon it was 10^{-8} m^2/s. This may be due to incomplete adsorption of phenols on activated carbon in 4 h. An equation analogous to Arrhenius equation was applied to calculate diffusion activation energy and entropy of activation. The results show that no significant change occurs in the internal structure of adsorbent during the adsorption of phenols.

Adsorption isotherm data were fitted to Langmuir, Freundlich, Redlich-Peterson, Radke-Prausnitz, Toth, and Fritz-Schlunder isotherm models. Statistical analysis showed that amongst six isotherms used, Langmuir gave the poorest fit with correlation coefficient (R^2) of 0.85-0.99, average % standard deviation (σ) of 3.27% and maximum percentage deviation of 41%. All other isotherms correlate data very well. The R^2 values for rest the models were more than 0.9. The σ values for Freundlich, Redlich Peterson, Toth, Radke Prausnitz and Fritz Schlunder were 2.84%, 2.23%, 2.63%, 2.23% and 2.28% respectively. The maximum adsorption capacity was found in the case of hydroxy phenols namely catechol and hydroquinone with all the adsorbents studied. Effect of -OH, $-NH_2$ and its position in the phenolic ring and solubility of phenols in water were found to affect the adsorption capacity.

Biological degradation and adsorption on activated carbon are used separately for removing phenolic compounds from wastewaters. Use of activated carbon entails prohibitive installation and

operating costs, and is energy intensive, whereas processes based on biological degradation are slow, sensitive to high phenol concentration, and pH. In the process called Bioactive Activated Carbon (BAC), the adsorption and biodegradation of phenols on the activated carbon have been combined. This process has been shown to be viable even for treating high strength phenolic wastewater. In this treatment option, a biological growth is encouraged on granular activated carbon (GAC) and both the removal mechanisms adsorption and biodegradation, when combined give better results. The bacteria are saved from the toxicity of high concentration of phenols by adsorption, whereas the service life of activated carbon is prolonged due to biodegradation of phenol remained in the liquid and that desorbed from the activated carbon. This process of regeneration of activated carbon is called bio-regeneration.

Phenolic compounds present in effluent may differ in their biodegradability and adsorb-ability. The literature survey revealed that most of the research work pertaining to biodegradation, activated carbon and the bioactive activated carbon has been conducted with only phenol as the target compound. Only few studies on other phenols are reported. Also, no literature is available on the removal of phenols using *Pseudomonas aeruginosa* on the bioactive activated carbon. The present research work has been focused to study the removal aspects of phenols namely phenol, 3-aminophenol, and catechol, using bioactive activated carbon system and biodegradation kinetics of these compounds with *P. aeruginosa* (ATCC 9027). The work also includes the adsorption studies of these compounds on activated carbon in presence of basal salt medium, which is required for the growth of bacteria. The slanted culture of *P. aeruginosa* was used and could be acclimatized to phenol, 3-aminophenol and catechol up to 800, 500 and 600 mg/l respectively. However, the same strain could not be acclimatized to as low as 50 mg/1 initial concentration of resorcinol. The well-acclimatized culture of *P. aeruginosa* degraded completely the phenol, 3-aminophenol, and catechol of initial concentration 800, 500 and 600 mg/l in 136, 160 and 85 h respectively. Time taken by the microbes to adapt themselves to the new environment and substrate is called lag phase. Further, batch growth studies indicate the presence of different lag phases at different concentrations of phenols. At higher concentrations, longer lag phase was observed. The trend of specific growth rate with initial concentrations showed that phenols are inhibitory compounds. Monod's and Linearized Haldane's model could not represent the growth kinetics over the concentration range studied. However, Haldane's growth kinetics could be fitted to the growth kinetics data well for the entire concentration range. Statistical analyses indicate that the maximum percentage deviation and the correlation coefficient for the fit of this model to the data of all the three phenols are less than 10% and more than 0.99 respectively. Further, the decay coefficients were determined as 0.0056, 0.007 and 0.0068 h^{-1} for growth on phenol, 3-aminophenol and catechol

respectively. Besides, the yield coefficient for growth on phenol, 3-aminophenol and catechol were found 0.53, 0.52 and 0.48 mg/mg respectively. The results obtained are presented in Chapter 4, 5 and 6.

Adsorption isotherm and kinetic studies for three phenolic solutions in Basal Salt Medium (BSM) on activated carbon at 30°C were carried out in similar manner as for adsorption with phenols without BSM (as explained in Chapter 3) in a batch reactor for 48 h. The three phenolic compounds showed the similar adsorption behavior. Approximately 50-60% of the ultimate adsorption capacity was realized within 1 h contact time of activated carbon with phenols. The adsorption capacities in presence of BSM of the three phenolic compounds were in the order: catechol >phenol > 3-aminophenol. The results on kinetic and rate controlling mechanism, isotherms, effect of mass of adsorbent, effect of contact time and initial concentration are similar to as for adsorption studies of phenols on fly ash and activated carbon without BSM as reported in Chapter 3.

The bacterial strain *P. aeruginosa* acclimatized to phenol, 3-aminophenol and catechol separately could be immobilized on activated carbon. Most of the bacteria were adsorbed within 18 h of contact and reached equilibrium in 24 h in all the three cases. The removal of phenol at initial concentrations of 800, 1000 and 1200 mg/l, of 3-aminophenol at initial concentrations of 500, 600, 700 mg/l and of catechol at initial concentrations of 600, 700 and 800 mg/l was complete, unlike biological degradation, where the phenol, 3-aminophenol and catechol could not be degraded beyond 800, 500 and 600 mg/l respectively. The removal of phenol and catechol started immediately without any lag phase. The photomicrograph of biofilm coated activated carbon indicated the presence of dense growth of bacteria mass in the pits and crevices, scattered bacteria over the smooth surface of activated carbon and those grown on the surface of the macro pores. The thickness of biofilms formed on the activated carbon has been estimated to be in the range 14-31 μm. The bio-regeneration study indicates that there was 33-66% regeneration of activated carbon in 48 h.

The application of advance oxidation process, which can completely mineralize phenolic waste to less hazardous substances, has been reviewed. Lot of research work is going on since it is the most promising ecologically. A very large number of research papers are available on photo oxidation. Therefore, in the present program through exhaustive literature review, an attempt to explain this technology, its various options (photochemical oxidation, photo-catalysis and photo-fenton) and effect of various parameters has been made. To make this technique economically feasible and of wide applicability, integration of this method with biological treatment and also

replacing UV radiations with the solar energy has been proposed. Only literature review is presented in this report. Experimental work could not be carried out beyond making experimental set up due to resource limitations.

The fly ash adsorption in place of activated carbon for treatment of effluents containing low to intermediate level of concentration of phenols may be employed. Bioactive activated carbon shall be useful in treating effluents containing high concentrations of phenols. Advance oxidation processes shall be useful in treatment of effluents containing low concentration of phenols to meet stringent regulations.

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