CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

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8.1 CONCLUSIONS

8.1.1 Use of Fly Ash as an Adsorbent

Removal of phenol and its derivates, namely catechol, resorcinol, hydroquinone, 2-aminophenol and 3-aminophenol using fly ash obtained from four different industrial sources have been studied using adsorption technique. The samples of fly ash were obtained from:

(i) Lignite based fly ash from Gujarat Industrial Power Corporation Ltd., Surat.

(ii) Coal based fly ash from Gujarat Electricity Board, Ukai.

(iii) Coal based fly ash from J.K. Paper Mill, Songadh.

(iv) Bagasse based fly ash from Sayan Sugar Industries, Surat.

These samples have been named as fly ash A, fly ash B, fly ash C and fly ash D respectively. The investigations to remove phenols from aqueous solutions by adsorption on these fly ash samples were carried out to determine:

- Effect of various parameters on adsorption
  - Initial concentration and contact time
  - Temperature
  - pH
  - mass of adsorbent
  - presence of salts
- Adsorption isotherm models that correlate the data namely Freundlich, Langmuir, Redlich Peterson, Radke Prausnitz, Fritz Schlunder.
- Thermodynamics and
- Kinetics of adsorption.

All the above mentioned studies were also done using activated carbon (IC 810) manufactured by Gujarat Industrial Carbon Pvt. Ltd., Ankleshwar, to compare the efficacy of these adsorbents (viz. fly ash from different sources and activated carbon) on different phenols.

The conclusions drawn from these studies are:

(i) Effect of initial concentration on adsorption of all the phenols on fly ash A, B, D and activated carbon were studied by changing initial concentrations from 25 ppm to 500 ppm at 30°C, 45°C and 60 °C. For fly ash C, initial concentration range of 25 ppm to 100 ppm was studied for all the phenols. Fly ash C has low adsorption capacity. Its surface area is also small. Therefore, the investigations on this fly ash were carried out at low initial concentration. The percent removal of all the phenols increases with the decreasing initial concentration, however, the amount of adsorbate adsorbed increases with increase in initial concentration nonlinearly.

(ii) Rate of adsorption is high in the initial period and slows down and then becomes constant. It has also been observed that the time to reach equilibrium is concentration dependent. An equilibrium time of 240 min was selected for all the systems for kinetic and equilibrium studies.

(iii) The effect of change in pH from 2 to 11 for all the phenols other than hydroquinone has been studied. For hydroquinone, the effect of pH on adsorption has been studied in the range of 2 to 7 due to tautomerism nature of hydroquinone in alkaline solution. It was observed that the uptake decreases as pH increases for all hydroxyl phenols. Whereas 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 complex behavior observed in case of aminophenols is attributed to the existence of different ionic equilibrium in aqueous solution at different pH.

(iv) The effect of amount adsorbent added on percentage removal was studied using 100 mg/l of initial concentration of all the phenolic solutions for all the fly ash A,B,C and D, where as for activated carbon 300 mg/l of initial concentration of all the phenols was taken. The increase in amount of adsorbent mass added increases the percentage removal and decreases the adsorption density. The optimum mass of adsorbent values for the adsorption of phenols on fly ash A, B and C is 2.5 g per 100 ml. For fly ash D and activated carbon, it is 1.5 and 0.5 g per 100 ml respectively.

(v) Addition of 1 M NaCl and 0.5 M Na_2SO_4 increases sorption rate and increases the adsorption capacity by 1to 3 %.

(vi) The decrease in temperature is found to be more favorable for the adsorption of phenols on all the five adsorbents (fly ash A, B, C, D and activated carbon). This indicates that adsorption of phenols on these adsorbent is exothermic.

(vii) 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 of the hydroxy phenols namely catechol and hydroquinone was found in all the cases. Effect of functional groups attached to benzene ring and solubility of the compound in water were found to affect the adsorption capacity.

(viii) Adsorption isotherm experiments were conducted for adsorption of all the phenols on fly ash A, B, D and activated carbon at 30°C, 45°C and 60°C, over a wide equilibrium concentration range (25 to 500 mg/l). For fly ash C, concentration range of 25 to 100 mg/l was used. The relative adsorbabilities of phenolic compounds is in the order for different adsorbents:

Activated carbon > fly ash D > fly ash B> fly ash A> fly ash C.

The surface area and carbon content of these adsorbents are in same order as their adsorbability. Thus we conclude that adsorbability depends on the surface area and the carbon content in the fly ash.

(ix) In the experiments to determine the kinetics of adsorption, the initial concentrations were varied from 25 mg/1 to 500 mg/1 with optimum mass of adsorbent for 4 h for fly ash A, B, D and activated carbon. For fly ash C, initial concentration was varied from 25 mg/l to 100 mg/l keeping all other conditions identical. Lagergren's pseudo first order kinetics and pseudo second order kinetics given by Ho and Mckay have been used 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.

(x) The rate of adsorption was found to be film and intra-particle diffusion controlled. Weber Morris plot was used to analyze the kinetic data for determining this rate-controlling step. From these plots, it was observed that there are three regions of change of rate of adsorptions, termed as rapid, medium, and slow. The values of effective diffusion coefficient, calculated using Vermeulen and Urano approximations were found to be of the order of 10^{-12} to 10^{-14} m^2/s for all the phenols on all the fly ashes. However for activated carbon it was 10^{-8} m^2/s, it may be due to incomplete adsorption on activated carbon in 4 hours. An equation analogous to Arrhenius equation was applied to calculate diffusion activation energy and entropy of activation. The results revealed that no significant change occurs in the internal structure of adsorbent during the adsorption of phenols.

8.1.2 Removal of Phenolic compounds using Bioactive Activated Carbon

The removal of phenol and its derivatives, namely catechol and 3-aminophenol, have been studied in bioactive activated carbon (BAC) systems. Bioactive activated carbon systems are mainly comprised of granular activated carbon (GAC) as adsorbent and an actively growing biofilm on it. The integration of these two modes of removal of impurities in aqueous solution has been found complementary to each other. The research work here is mainly divided in three parts; (I) biodegradation studies, (II) adsorption studies in presence of nutrients for bacteria and (III) bioactive activated carbon system as a single unit. All the experiments were performed in batch mode. The conclusions arrived at are given below:

(I) Biodegradation:

The biological removal of phenol, 3-aminophenol and catechol were studied using *P. aeruginosa* (ATCC 9027) in batch reactor at 30°C. The Basal Salt Medium (BSM) was used as aqeous growth medium for bacteria. Main conclusions are as given below:

(i) The bacterial strain *P. aeruginosa* could be acclimatized to phenol, catechol and 3-aminophenol up to 800, 600 and 500 mg/l concentration respectively. Above these concentrations, the culture could not acclimatize.

(ii) The results of batch degradation of phenol showed that the initial phenol concentration of 800 mg/l of phenol was fully degraded in 136 h. Where as in case of 3-aminophenol, 500 mg/l initial concentration could be completely degraded in 160 h. In case of catechol 600 mg/1 initial concentration could be completely degraded in 85 h.
Different initial phenol (25-800 mg/1), 3-aminophenol (25-500 mg/l) and catechol (25-600mg/1) concentrations were taken for studying the effect of concentration on biodegradation behavior. In case of all these compounds, different lag phase was observed at different concentrations. The higher the concentration, the longer the lag period was observed.

(iii) The growth of *P. aeruginosa* is inhibited by phenol, 3-aminophenol and catechol. In the cases of phenol and catechol, specific growth rate data from low concentration region only could be represented by Monod's growth kinetic model, whereas the specific growth rate data from high concentration region could be represented by Linearized Haldane's growth kinetic model. In case of 3-aminophenol, Monod's growth kinetic model could not be applied. However, Haldane's growth kinetic model could fit the specific growth rate data of *P.aeruginosa* on all three phenols quite well over the concentration range studied. Statistical analyses indicate that the maximum deviation and the correlation coefficient, R^2 for the fit of this model to the data of all the three phenols are less than 10 % and more than 0.99 respectively.

(iv) The values of the endogenous or decay coefficient were determined from endogenous phase of growth curves as 0.0056, 0.007 and 0.0068 h^{-1} for phenol, 3-aminophenol and catechol respectively. Further, the values of yield coefficient were determined as 0.53, 0.52 and 0.48 mg/mg for phenol, 3-aminophenol and catechol respectively.

(II) Adsorption in Basal Salt Medium:

Adsorption isotherm and kinetic studies for three phenolic compounds on activated carbon in Basal Salt Medium at 30°C were carried out in similar manner as discussed before in batch reactor for 24 h. In kinetics and equilibrium experiments, the initial concentrations were varied from 100 mg/1 to 800 mg/1 with fixed carbon dose of 2.5 g/1. Given below are findings of these studies:

(i) The three phenolic compounds showed the similar adsorption behavior. Approximately 50-60% of the ultimate adsorption capacity was realized within 1 h of contact with phenol, 3-

aminophenol and catechol. The adsorption capacities of the three phenolic compounds were in the order: catechol >phenol > 3-aminophenol.

(ii) The kinetics and rate controlling mechanism, isotherms, effect of mass of adsorbent, effect of contact time and initial concentration are similar as described under Chapter 3 on adsorbent studies of phenols on fly ash and activated carbon in absence of basal salt medium(BSM). The presence of BSM does not affect the adsorption behavior of phenols.

(III) Bioactive Activated Carbon:

The bacterial cells of acclimatized *P. aeruginosa* were immobilized on activated carbon. The removal of phenol and catechol by using this biofilm coated activated carbon in Basal Salt Medium was studied by contacting in batch reactor. The main conclusions of this study are as follows.

(i) The bacterial strain, *P aeruginosa* acclimatized to phenol, 3-aminophenol and catechol separately could be immobilized on activated carbon. In terms of immobilization behavior, the trend was same in all the three phenols and most of the bacterial cells had adsorbed on activated carbon within 18 h of contact.

(ii) The removal by BAC of phenol at initial concentrations of 800,1000 and 1200, of 3-aminophenol at initial concentrations of 500, 600 and 700 , and of catechol at initial concentrations of 600,800 and 1000 mg/1 was complete at all concentrations in all the cases. Whereas by biodegradation alone the phenol, 3-aminophenol and catechol could not be degraded beyond 800, 500 and 600 mg/1 respectively. Initial rapid removal by adsorption followed by slow biodegradation of phenols was observed at all concentrations. No lag phase was observed during the biodegradation of these three phenolic compounds.

(iii) Photomicrographs of virgin carbon clearly show the rough surface of activated carbon, where bacteria may be protected from the shearing action of flow of fluid around the activated carbon particle. Further, the examination of photomicrographs of activated carbon particles coated with biomass reveals the dense growth of bacterial mass in pits and crevices, scattered bacteria over the smooth surface of activated carbon.

(iv) The thickness of biofilm formed on the activated carbon, when the removal of phenol (800 mg/1), 3-aminophenol (500 mg/l) and catechol (600 mg/1) was complete, was in the range 14 to 34 μm. This is the particle average film thickness.

(v) Only 33 to 63% bio-regeneration took place.

8.2 RECOMMENTATIONS FOR FUTURE WORK

(i) The result of the present study suggests that adsorption on fly ash from different sources can remove phenol, catechol, resorcinol, hydroquinone, 2-aminophenol and 3-aminophenol efficiently, even when fly ash has not been activated using steam or acid. Full capacity of adsorbent is not realized in batch operation. Similarly, bioactive carbon system is capable of removing phenol, 3-aminophenol and catechol. The continuous column studies (experimental as well as theoretical) on these systems may be carried out. The results of these studies would be of great help for the design of large-scale treatment plants.

(ii) In adsorption studies on fly ash, regeneration or bio-regeneration or recovery of adsorbate may be investigated to crystallize this approach for industrial application.

(iii) Fly ash adsorption may be studied by carrying out adsorption and biosorption in combination with activated carbon.

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