Oxidation of Cyanide and Phenol by Ozonation Process

by

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Thesis submitted in fulfillment of the requirement for the award of the degree of

Doctor of Philosophy

To the

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dedicated to

my

late mother

CERTIFICATE

This is to certify that the thesis entitled " **Oxidation of Cyanide and Phenol by Ozonation Process** " has been submitted by Mr. Mrityunjay Pandit to I.I.T Delhi, for the award of the degree of ***Doctor of Philosophy*** in **Chemical engineering**, is a record of bonafide research work carried out by him. Mr. Pandit has worked out under my guidance and supervision and has fulfilled the requirements for the submission of thesis which to my knowledge has reached the requisite standard. The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any Degree or diploma.

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ABSTRACT OF THE THESIS

Title: ***Oxidation of cyanide and phenol by ozonation process.***

Abstract: The highly toxic cyanide and phenolic compounds are found in many industrial effluents. Complete detoxification of these compounds should be done before discharging the effluents. In the present study the detoxification of cyanide and phenol by ozone has been studied. For this purpose a laboratory scale ozonator has been designed, fabricated and installed in the laboratory for ozone production. The reaction kinetics of ozone-cyanide and ozone-phenol has been investigated using a known interfacial area reactor, i.e, stirred contactor. Experiments were also carried out in a bubble reactor to study the effect of different operating process parameters such as gas flow rate, pH of the solution, catalytic effect of Cu and Fe ions, effect of the presence of any solutes in the reaction mixture such as sodium chloride, sodium sulfate etc.

The analysis of the experimental date from the stirred reactor indicate that the reaction of ozone and cyanide in aqueous solution can be regarded as a pseudo fast reaction in the pH range of 7.5 to 11.0. The reaction follows first order relationship with respect to both cyanide and ozone concentration. The overall second order rate constant at different temperature and pH has been calculated. The pseudo fast reaction also implies the importance of mass transfer resistance of the ozone oxidation process. It has been observed that the second order rate constant of the ozone cyanide reaction increases with the increase of the pH of the solution. The rate constant also increases with increasing temperature of the solution and follows Arhenius correlation. The activation energy at pH 10.5 was found

17.25 Kcal/g. mol.

The reaction between ozone and phenol in aqueous solution was also found to be a pseudo fast reaction. The reaction rate was found to be first order with respect to both ozone and phenol. The second order rate constant was calculated at pH 5.0 and 8.0. It has been observed that the rate constant is strongly dependent on the pH of the solution and increases rapidly at higher pH values. It was observed that at alkaline solution the rate of reaction is almost ten times higher that in acidic solution. At pH 10.0 the reaction was found to be nearly instantaneous. The activation energy was calculated at pH 8.0 and its value is 8.97 Kcal/g. mol.

The results obtained from the bubble column experiments indicate that ozone can be used as a very effective oxidation reagent for the total detoxification of cyanide and phenol. The ozone cyanide reaction is a two step process. First ozone reacts with cyanide to form cyanate and later ozone reacts with cyanate to form carbon dioxide and nitrogen. Generally 1-1.2 moles of ozone is required per mole of cyanide. It was also observed that the rate of cyanate oxidation is slow compared to cyanide oxidation. For ozone phenol reaction, ozone first reacts with phenol and produces by products which are further oxidized and finally produces carbon dioxide and water. Average 4-6 moles of ozone are required for each mole of phenol. Detailed analysis of the reaction system showed that the oxidation of cyanide and phenol by ozone is controlled by mass transfer resistance in liquid phase. Hence the reactor system of gas-liquid contactor will have to be designed with high specific surface area per unit volume along with a intensive turbulence in the liquid medium. The rate of oxidation of both cyanide and phenol increases with increasing ozone partial pressure and gas flow rate. It was also observed that at higher pH of the solution The rate of oxidation of cyanide and phenol increases. Thus it is advisable to operate the ozonation process at higher pH (the optimum pH for the reaction is 10 to 11) to take the advantage of higher reaction rate. Copper ions can catalyze the reaction of cyanide reaction. Similarly ferric oxide enhances the phenol oxidation rate. For design purpose the presence of the inorganic solutes should also be considered for both cases, because they also affects the reaction rate.

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