Treatments of Effluent from Resin Industry by Hybrid Reverse Osmosis System

Jaymin Patel[1], S.M. Dutta[2]

1. *Student, Chemical Engg. (CAPD) LDCE, Ahmedabad, Gujarat, India*
[2]*Associate Professor, Chemical Engg. Dept., LDCE, Ahmedabad, Gujarat, India*

ABSTRACT

Phenol and phenolic compounds are among the most prevalent forms of organic chemical pollutants in resin industrial wastewaters. Therefore, treatment of those wastewaters is required before final discharge to the environment. Among the different processes described for removal or degradation of phenolic compounds, hybrid processes that combine pressure driven membrane processes with adsorption processes have been developed. In order to optimize those phenol concentrations, a detailed study of the effectiveness of the resin bed and membrane process step is necessary. A study of phenol, BOD, COD, TDS removal from aqueous solutions by hybrid reverse osmosis using different experimental conditions (feed phenol concentration,Quantity of XAD-4 Resin, pressure and pH) and different R.O. membranes (polysulfonate, polyethylene, cellulose acetate, nitro cellulose, polyacrilonitrile, polyamide, PTFE, PVF) is carried out in this paper. The water and phenol removal efficiency have been obtained accordingly to the treatment for maintaining ZLD (Zero Liquid Discharge).

Key words:*Phenol, Wastewater, Adsorption, XAD-4 resin, Oxidation, Reverse osmosis, Membrane Process.*

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1) INTRODUCTION

A research conducted in USA about the presence of organic contaminants in streams shows that 80% of those streams contained organic contaminants. Phenol and phenolic compounds are among the most prevalent forms of organic chemical pollutants in industrial wastewaters. Industrial processes such as oil refineries, petrochemical plants, ceramic plants, steel plants, coal conversion, Resin industry plant (Phenol Formaldehyde Resin), and pharmaceutical industries, generate aqueous effluents containing high concentrations of phenol and other compounds. Phenol is potential human carcinogen and is of considerable health concern, even at low concentration [1]. Acute poisoning can lead to severe gastrointestinal disturbances, kidney malfunction, circulatory system failure, lung edema and convulsions Fatal doses can be absorbed through the skin. Key organs damaged by chronic phenol exposure include spleen, pancreas and kidneys [1]. Careful treatment of wastewater containing phenol and phenolic compounds is then required before final discharge to the environment. Many technologies have been investigated for removing and degradation of phenolic compounds in wastewater. They included adsorption [2], enzymatic treatments [3], and oxidation [4] and combined techniques [5].

Many studies have been performed on the separation of organics and organic pollutants by RO membranes, and these studies have identified some of the unique aspects associated with organic separation. In an earlier research they have compiled separation and flux data of cellulose acetate membranes for a large number of organic compounds, including many organic pollutants. They found that organic separation can vary widely (from <0% to 100%) depending on the characteristics of the organic (polarity, size, charge, etc.) and operating conditions (such as feed pH, operating pressure, etc.). Rejections varied considerably for the different solutes, and rejections of ionizable organics were greatly dependent on degree of dissociation; non-ionized and hydrophobic solutes were found to be strongly adsorbed by the membranes and exhibited poor rejection.

Many methods, such as oxidation, precipitation, adsorption, ion exchange and solvent extraction have been used to remove phenolic materials from aqueous solutions. The RO separation of an organic solute from aqueous solutions is of interest from the point of view of its application for wastewater treatment and water pollution control [3]. Membrane processes can be used to remove phenol from water, but they are not always successful [4]. Therefore, increasing attention is being paid to the study of various chemical and physical processes to accompany such separation systems. In general, depth filters, GAC, microfiltration and ultra-filtrationare used to reduce the pollution loading for RO systems. If the capability of a RO membrane module for phenol removal is to be investigated, such pre-treatment methods must be considered. Thus, the objective of the following study is to investigate phenol removal by two pretreatment methods and RO under different conditions.

2) MATERIALS AND METHOD

2.1 Experimental set-up of Resin Bad Reactor

The experiments were conducted on pilot-scale apparatus (Figure 1). XAD-4, a nonionic polymeric resin composed of polystyrene chains cross- linked with divinylbenzene, was used as the adsorbent for studying the adsorption behavior of various Phenols contain industrial waste water [16]. The medium size of the resin is 35–40 mesh or 0.02 inch. The specific surface area, average pore volume, and average pore diameter were determined to be $820m^3/g$, $0.81cm^2/g$, and 23.8 Å, respectively.

For the adsorption equilibrium experiments, predetermined amounts of XAD-4 resin were introduced into resin bed reactors filled with resin balls of known concentrations of phenol and the whole reaction setups were maintained at 30±5◦C. The solution pH was adjusted to desired level (between 3 and 11) by adding acidic or alkaline solutions to the collection tank. the waste water distribution continues on the resin balls. After 40-50 minutes of contact time for resin balls and phenol-containing waste water, the solution pH was recorded and the resin balls was allowed to pass remaining water from the percolated tray. The mesh size of that tray is less than 0.02 inch. The solution pH was recorded, and the concentrations of various phenols in the filtered samples were determined by measuring the absorption of specific wavelength with a UV-160A UV/visible spectrophotometer. Experiment performed for different resin balls quantity and found the best efficiency of waste water recovery.

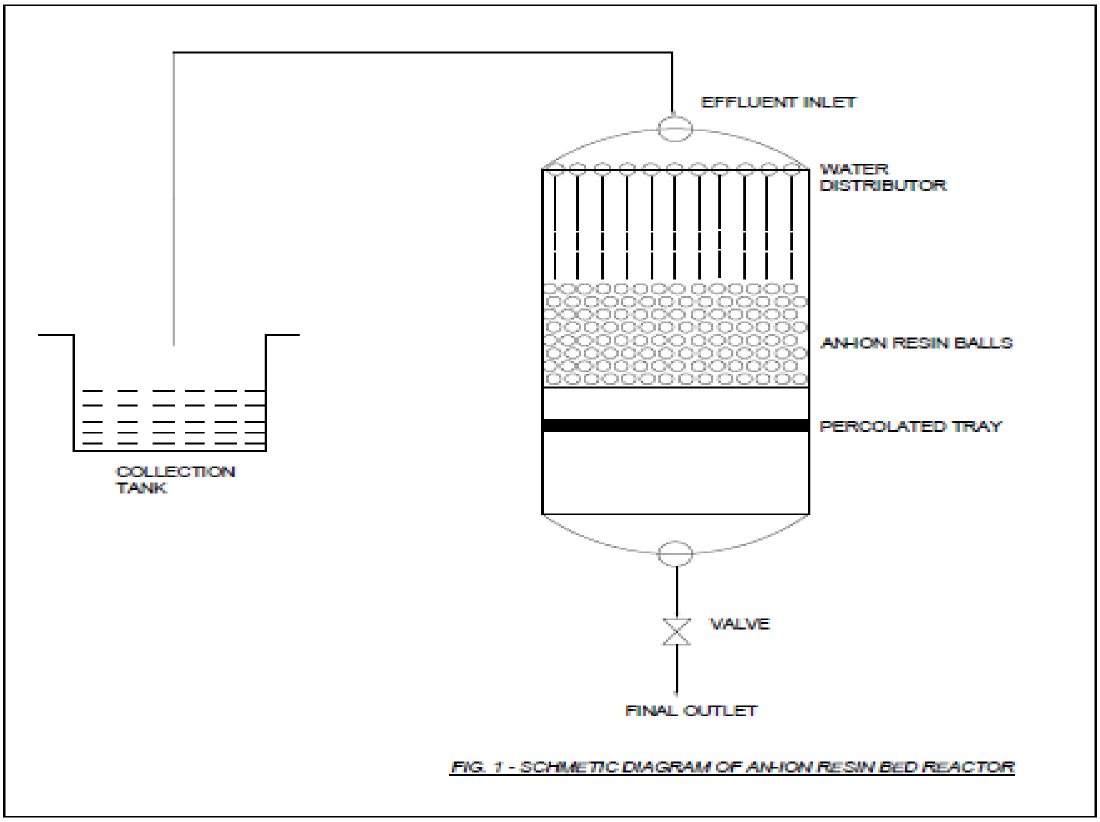

Figure: 1- Schematic Diagram of Non-Ion Resin Bad Reactor

2.2 Regenerating an ion-Exchange Resin

As stated earlier, an ion-exchange resin in industrial use is usually regenerated every 12 to 48 hours. Depending on the use of the resin, this can be done in several different ways, each with their own advantages and disadvantages depending on both chemical and economic factors [9].

Regeneration is important because reducing the regenerate level lowers water quality by allowing a small proportion of the ions which are being taken up by the resin to slip through without exchange. For example, with twin bed deionizers, incomplete regeneration of the cat-ion resin to the hydrogen form allows leakage of some sodium (the least held of the cat-ions commonly found in natural supplies) into water passing to the anion exchange vessel [6]. Consequently, the water leaving the anion unit still contains this sodium in the form of sodium hydroxide solutions usually of pH 8 to 9. However, the excessive amounts of regenerate required for complete regeneration means that this is rarely practical. In practice a compromise is usually reached, and commonly resins are regenerated to about two thirds of the total capacity. In addition, for many uses total purification is not necessary. For example, the water with a pH of 8 to 9 mentioned earlier is highly suitable for use in boilers, as they require slightly alkaline water.

Some impurities such as silica can only be removed by a strongly basic resin. For example, dissolved silica is a major component of most water supplies. Normally it exists as a neutral polymer, and it becomes negatively charged only at high pH levels. This means that it can only be removed from water in the highly alkaline environment of a strong base resin in the hydroxyl form.

The exchange process is often made more efficient by introducing the regenerant at the bottom of the resin column and passing it upwards through the bed (counter current regeneration). This ensures that the resin at the bottom becomes more highly regenerated than that above it. Treated water leaving the column flowing downwards then comes in contact with this resin last and undergoes the highest possible degree of exchange.

2.3 Advantages and Disadvantages in the use of Ion-Exchange Resins

The advantages of ion exchange processes are the very low running costs. Very little energy is required, the regenerant chemicals are cheap and if well maintained resin beds can last for many years before replacement is needed. There are, however, a number of limitations which must be taken into account very carefully during the design stages. When these limitations itemized appear to represent a formidable list and the impression can be given that ion exchange methods might have too many short comings to useful in practice. However, this is not the case as the advantages mentioned above are very great and compensation can readily be made for most restrictions.[7]

2.4 Experimentation with hybrid R.O. System

The whole experiment performed on Laboratory base. The resin industry waste water containing different characteristics i.e. pH, Phenol, COD, BOD, TDS, TSS. Treatment of that waste water is necessary. Predetermined quantity of waste water and resin has been taken. The development for phenol removal techniques carried out with XAD-4 Resin, carbon filter used for the color removal with BOD and COD removal of minimum percentage. For the high range of BOD and COD, secondary treatment is necessary with high pressure aeration system (pressure=2 atm).After the aeration system the effluent should be introducing onto U.F. Membrane for TSS removal. The RO system was assumed for high range of TDS Removal. During 60 seconds at the beginning of experimental studies. Then the experimental was operated normally. The flows were regulated and the concentrate stream was recycled to the feed tank. The Permeates from the RO were collected in another tank and the parameters was measured. The RO rejected were use in gardening purpose or it should be evaporated based on its characteristics. After each experiment, the RO membrane was washed with distilled water. The pH and conductivity of all samples were measured. The Hybrid R.O system experimental result shown in **Table: 2**.

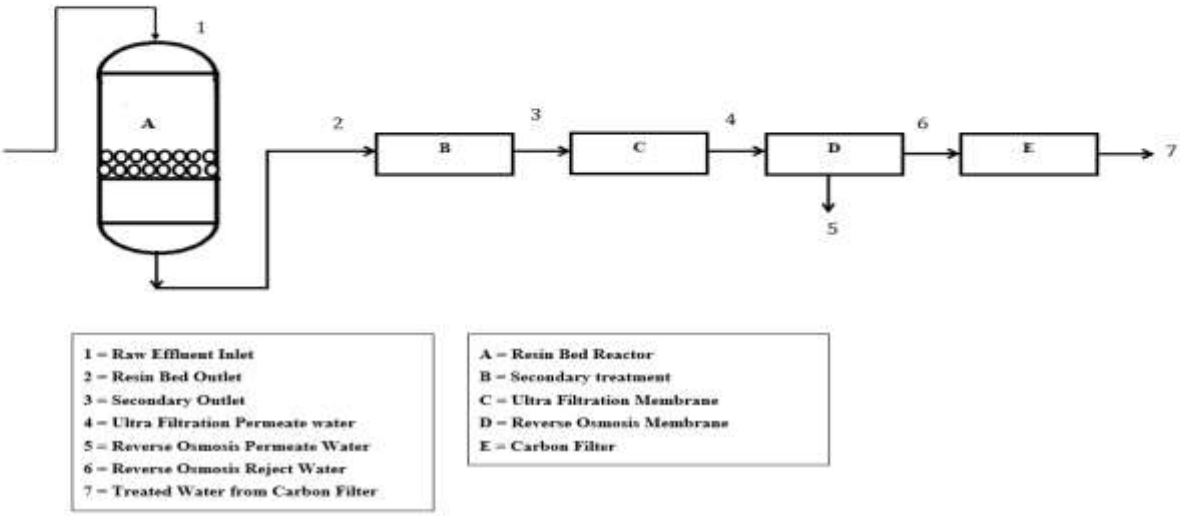

Figure: 2- Schematic Diagram of Hybrid R.O.System

3) RESULTS AND DISCUSSION

3.1 Effect of initial concentration

The effect of the initial phenol concentration on the removal efficiency is plotted in Fig. 1. In this study phenol concentration was varied between 1 to 107 mg/ L and the resins dosages were kept at 100 gm/L to 1000gm/L. Results show that phenol ions removal through resins is considerably influenced by its concentration in the feed stream. It was found that the phenol removal from 107 mg/L (Initial) from 1-3 mg/L phenol in the outlet stream, to 99.7 % for the highest assayed concentration under identical XAD-4 operating conditions in terms of recirculation time and temperature for the strong non -ion exchange resin. In this case, it can be ensured that XAD-4 was the predominant process responsible of the phenols ion removal since the increase in Resin Quantity in the outlet stream was directly proportional to the removal efficiency for each assayed initial concentration. Hence, the decrease in the removal percentage with the phenol concentration in the feed stream could be related to saturation of the XAD-4 resin. The experiment result shown in **Table: 1**.

Table 1: Result of Experiment on Resin Bed Reactor

Sr. No.	Weight of Non-Ion Resin taken (gm)	Initial Phenol Concentration (mg/L)	Final Phenol Concentration (mg/L)	Percentage Removal (%)
1	100	90	25.20	67.32
2	200	107	23.50	81.85
3	300	97	18.36	79.19

4	400	99	11.99	87.12
5	500	101	9.40	91.50
6	600	102	5.40	96.49
7	700	98	1.53	96.50
8	800	99	1.28	97.72
9	900	100	1.10	98.90
10	1000	101	1.20	99.78

Figure 3 shows the removal of phenol over a pH range of 4-9 by RO in the presence of pre-treatment, thus showing the phenol removal capability of the Resin bad. Phenol removal increases with an increasing quantity of resin balls, particularly when it was above 700 gm to 1000 gm. increasing in phenol removal was very nearly. The variation in pH from 4 to 6 increases the removal efficiency slightly, i.e. from 67% to 87%, but it fell dramatically to 99% at pH 6.5. It was found that the best removal by XAD-4 Resin alone occurred in the range of pH 4-7.

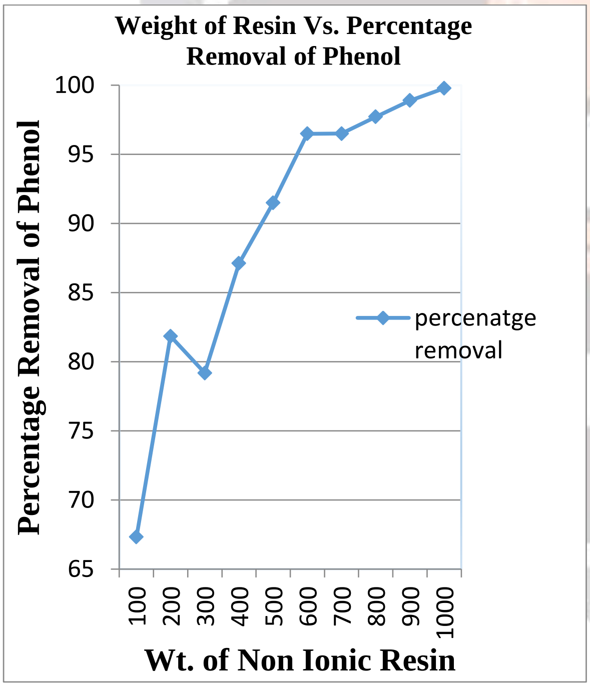

Figure: 3: Effect of Weight of Resin balls to Phenol Removal

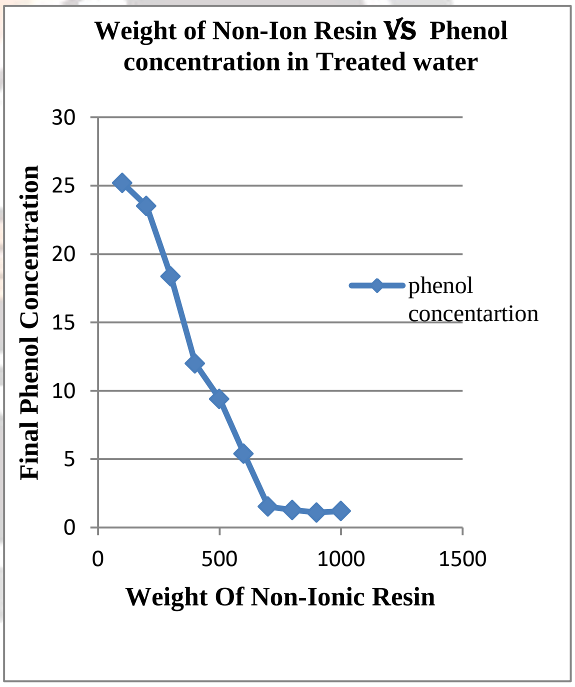

Figure: 4: Effect of Non-Ionic Resin to Phenol Concentration

The phenol concentration in the influent was kept at 107 mg/l. After the application of XAD-4 resin, the phenol concentrations in the effluent varied from 107 mg/l to 1 mg/l, depending on the pH. When the pre-treatment methods, i.e. the XAD-4 Resin bad, are incorporated, the overall efficiency of the RO increases. The variation of phenol rejection with feed concentration, pressure and pH for the three membranes is represented. Poor rejections are obtained in all cases, with polyamide membranes showing better results. It has been suggested that for the removal of high value of BOD and COD the secondary treatment is required before treating effluent in the R.O. Pressure increase leads to a significant decrease of BOD and COD rejection. There are some factors related to the molecular characteristics of organic molecules (solubility, acidity, ability to hydrogen bonding, etc.) that affect their rejection by reverse osmosis membranes. Those factors favor organic solutes like phenol to be sorbed into the membranes and to be more easily transported across them, leading to low rejection values. The consistency for removal of TDS and TSS, the U.F. Membrane was installed and finally the remaining characteristic water treated by R.O. membrane and got effective result.(As per State pollution control board).

Table 2: Result of Experiment on Hybrid R.O. System

Sr. No.	**Stream No.**	**1**	**2**	**3**	**4**	**5**	**6**	**7**
	Parameter (mg/L)	**Raw Effluent**	**Resin Bed Outlet**	**Secondary Outlet**	**U.F. Permeate**	**R.O. Permeate**	**R.O. Reject**	**Carbon Filter Outlet**
1	**pH**	**6.2**	**6.4**	**6.4**	**7.1**	**7.0**	**6.5**	**6.9**
2	**Phenol**	**102**	**1.2**	**NIL**	**NIL**	**NIL**	**NIL**	**NIL**
3	**COD**	**129600**	**58320**	**1166**	**315**	**95**	**150**	**70**
4	**BOD**	**32100**	**18900**	**380**	**95**	**24**	**41**	**30**
5	**TSS**	**130**	**130**	**110**	**90**	**9**	**2**	**1**
6	**TDS**	**8600**	**8600**	**8600**	**7740**	**1700**	**4000**	**2040**

5. Conclusion

Hybrid processes have been developed for treatment of waste water of resin industry combining adsorption and RO. Experiments has been conducted with Non-Ionic Resin bed reactor for phenol removal. The high quantity of resin balls removes high amount of phenol. At 700 gm optimum removal of phenol was achieved. No significant removal after that was noted. Adsorption with XAD-4 resin has given 99.7% removal of phenol from waste water with the help of weight of resin balls. In order to optimize, the concentration of phenol, TDS, BOD and COD hybrid processes were determined, a detailed study of the effectiveness of the membrane process step is necessary. A study of phenol removal from aqueous solutions by reverse osmosis using different experimental conditions (feed phenol concentration, pressure and pH) and different membranes has been carried out in this paper. Good rejections are obtained in all cases, with polyamide and cellulose acetate membranes showing better results. Some factors related to molecular characteristics of phenol, such as solubility, pH, BOD, COD rejection were determined. Good significant differences have been found on phenol rejection coefficients at different feed phenol concentrations and feed pH. Finally, phenol removal with its related characteristics were within the limit of state pollution control board norms.

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