INDUSTRIAL WASTEWATER TREATMENT - REMOVAL OF ACID FROM WASTEWATER

Sorokhaibam Laxmi Gayatri, Bhandari Vinay M. * and Ranade Vivek V.
Chemical Engineering and Process Development Division, National Chemical Laboratory,
Pune, Maharashtra (INDIA)

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ABSTRACT

Environmental pollution due to hazardous organic acid pollutants such as phenolics and carboxylic acids in industrial wastewater streams is a serious concern from environmental pollution point of view. The nature of pollutants and their concentrations vary substantially for different effluents and devising a suitable treatment methodology for these dilute streams is a challenge, many times, unique to specific industry due to the difficulties in bringing down the concentrations to meet very low statutory limits for the protection of the environment. In the present work, we report the studies on removal of acidic pollutants mainly carboxylic acids and phenolics. A review of different methodologies for the removal of acids indicates that adsorptive processes are best suited for removal as well as recovery of valuable acids. However, when the concentrations are very low and removal of the hazardous organics is essential, destructive methods for mineralization of acids such as hydrodynamic cavitation can be possibly and favourably considered as against conventional methods such as adsorption/ ion exchange. Experimental studies have been carried out for removal of organic acids using hydrodynamic cavitation employing vortex diode as cavitating device. Newer device such as vortex diode has been found to be substantially useful in reducing organic pollutants from wastewater streams and the extent of removal depends strongly on pollutant species. A new methodology of process integration combining hydrodynamic cavitation and adsorption is expected to have wider applications in mitigating environmental pollution in chemical industries.

Key Words: Acid removal, Hydrodynamic cavitation, Environmental pollution, Vortex diode, Wastewater treatment

INTRODUCTION

Industrial wastewater treatment is practiced using a number of physical, physico-chemical and biological methods of treatment. Quality of wastewater in terms of number and nature of pollutants, usually expressed in terms of Chemical Oxygen Demand (COD) and desired level of reduction in these pollutants dictates the selection of process. However, to determine the overall goals of the treatment process, it is necessary to evaluate removal, recovery as well as water recycle and reuse options, as water conservation is most pertinent in today’s context, in view of water scarcity. In this regard, wastewater processing requires many a times combination of different methods as single method of separation is seldom satisfactory. This can be accomplished using physico-chemical and biological methods, either alone or in combination. The treatment processes such as coagulation, adsorption, ion exchange, oxidation, membrane separations, cavitation etc. and / or biological methods mainly perform task of major removal of pollutants from the effluent. In the present study, we report technologically advanced but less practiced methods of wastewater treatment such as adsorption/ ion exchange and cavitation for the treatment of wastewaters containing weak organic acids. Some new insights have been obtained in the removal of refractory pollutants that are difficult to degrade / remove using conventional methods.

Treatment of wastewaters containing acids

Wastewaters containing acids, both inorganic and organic acids (carboxylic and phenolics)
are often encountered and this has been a challenging problem for over four decades. Removal of these pollutants require strategies involving, ion exchange, adsorption, solvent extraction, membrane separation, reactive distillation, reactive extraction, membrane based solvent extraction, emulsion liquid membrane separation etc. Ion exchange resins, in general and weak base resins, in particular, are most commonly employed for lower concentrations. Wastewater streams containing low concentrations of acids are invariably encountered in acid manufacturing plants, industries where acids are used as raw material or as catalyst, fermentation processes, metal plating industries etc. The concentrations range from 0.5 to 4%, depending upon the source of generation. Since, large volumes are to be treated that contain low concentrations of acids, the primary goal in such cases is largely removal of acids from the solution and not separation with objective being reduction in COD of wastewater to meet prescribed limits. There have been a number of experimental and theoretical studies on removal of acids and waste water treatments. Weak base resins have been recommended due to their high capacity of removal and ease of regeneration. It has also been suggested that the resins with high basicity are more suitable in wastewater treatment as total sorption of acids corresponding to theoretical resin capacity, especially for stronger acids can be achieved even at low acid concentrations. However, basicity effect depends on type of acid and for removal of weak acids such as phenols and cresols, both capacity of the resin and basicity of resin are equally important considerations in selection. Extraction has problems in wastewater treatment due to low concentrations of acids and also due to solvent contamination that can be a treatment problem in itself. Extraction studies in presence of inorganic acids and inorganic salts have also been reported for the recovery of carboxylic acids by Ingale and Mahajani. However, in most cases separation factors were not large. Solvent extraction is not attractive mainly because many problems are still unresolved with respect to proper selection of solvent and solvent recovery due to high affinity of acids for water. Adsorption / ion exchange and solvent extraction can be used for removal and recovery of the acids, while destructive methods such as oxidation, cavitation can be used to eliminate these pollutants from dilute wastewater solutions. In cases where stringent pollution control norms are to be adhered, cavitation technology can be useful as extreme conditions of pressure and temperature can break down pollutants and organic molecules to bring down COD to desired levels.

AIMS AND OBJECTIVES

The main aim of the present work is to investigate the performance of hydrodynamic cavitation and adsorption technique for removal of acids and phenols and to evaluate efficacy of treatment methodology in reduction of COD for industrial wastewaters.

MATERIAL AND METHODS

Experimental

All chemicals viz. phenol, 4-aminophenol and p-aminobenzoic acid used in the work were A. R. Grade and obtained from companies of repute. The adsorbents- Shirasagi GH2x, SRCx and TAC were obtained from Japan Envirochemicals Ltd. Japan, while adsorbent Norit was obtained from Sigma-Aldrich. Batch experiments were carried out on synthetic wastewater solutions using predetermined quantity of adsorbent and equilibrating with known quantity of solution and concentration. Cavitation experiments were carried out using 20 liters of synthetic wastewater solutions of known concentration and predetermined pressure drop and reactor conditions, details of which are given in later section. Spectroquant TR 320 digester of Merck make was used for digestion of the wastewater samples at 140°C for 120 minutes. After digestion, the samples were analyzed for COD reduction and absorbance on Spectrophotometer (spectro quant pharo 100 - Merck India). Removal / degradation of phenol / p-amino phenol / acid samples were analyzed on the basis of COD measurements. Adsorption in acid removal from wastewaters

Adsorption is a well established separation process in chemical industry and in wastewater treatment and activated carbons are commonly
used adsorbents. Adsorbents can be derived from range of raw materials (natural to synthetic polymers) are available in variety of forms ranging from powdered materials to nanomaterials, single or composite and are sold as inexpensive materials to highly expensive adsorbents depending on the type and nature of adsorbent. In wastewater treatment, adsorption is mainly used for removal of organic pollutants, metal removal and for colour removal applications. Adsorbents need regeneration and in most cases this is usually carried out using thermal, steam, solvent extraction, acid/ base treatment or chemical oxidation. Activated carbons can be a very good adsorbents especially for adsorption of pollutants from pesticides, herbicides, aromatics, chlorinated aromatics, phenolics, organics and soluble organic dyes, practically covering majority of industrial wastewater treatment requirements, though there is some limitation in removal for low molecular weight or high polarity compounds.9

In view of the qualities described above, adsorption finds widespread use in the treatment of wastewaters of most industries e.g. petrochemical, chemicals, pesticides, dyes and textiles, pharmaceuticals, food, inorganic mineral processing etc.

In the present work, four different carbon based adsorbents, some with modified surfaces, have been selected for treatment of wastewaters containing acid, mainly phenolics. The adsorbents have been characterized for the surface area, pore size and pore size distribution apart from the nature of surface modification. Batch experiments have been performed on synthetic wastewaters containing phenol, p-amino phenol and p-amino benzoic acid to evaluate efficiency of these adsorbents in removal of COD from wastewaters.

Removal of ammoniacal nitrogen and nitrogen compounds is an important and difficult problem in the wastewater treatment. Therefore, pollutants with nitrogen containing groups have also been selected for this work.

**Cavitation technology in wastewater treatment**

Cavitation can simply be defined as a physicochemical process employing oxidation mechanism coupled with physical breakage/thermal decomposition using cavitating device for degradation of chemical species. It proceeds through three main steps:

1. Formation of cavities with the help of cavitating device
2. Growth of cavities in the space provided by the cavitating device
3. Collapse of the cavities

On the basis of cavity creation mechanism, four types of cavitation can be defined.

1. Acoustic cavitation- use of sound waves
2. Hydrodynamic cavitation- hydrodynamic devices producing pressure drop
3. Optic cavitation- use of laser
4. Particle cavitation- through bombardment of particles

The nature of cavitating device controls the quantity and quality of the cavities formed. The cavities, when collapse, release large amount of energy which is used for generating oxidizing agents in wastewater. Subsequent to this step, series of radical reactions occur with complex organic matter present in wastewater leading to destruction of contaminants and also decolourisation of wastewater. The size, shape, growth and implosion of cavity are strongly dependent on the parameters such as nature and type of effluent, bulk fluid temperature, pH, salts, dissolved solids and reactor configuration. For all practical purposes, as of today, only acoustic and hydrodynamic cavitation can be considered to be most relevant for wastewater treatment. While acoustic cavitation requires ultrasound type sound waves for generating cavity in the bulk liquid, hydrodynamic cavitation utilizes constriction such as orifice/v Venturi/ vortex diode in the path of flow of fluid.10,11 The cavitating device of hydrodynamic cavitation is required to offer sudden pressure drop below vapour pressure of the liquid so that the liquid flashes into vapour, generating cavities. The number and size of cavities along with mechanism of collapse of cavities determine performance of the cavitation process. The collapse of cavities is important as it creates highly localised extreme high temperature and pressure conditions and consequently hydroxyl radicals and it is believed that the conditions vary depending upon the type of cavitating device. Thus, the design of cavitating device is...
important for efficient degradation of molecules. Strong oxidizing conditions with active chemical radicals and hydrogen peroxide are expected due to local high pressures (up to 1000 – 5000 atm.) and extremely high temperatures (up to 15000 K). However, the overall liquid medium remains close to ambient conditions in the smaller duration of the process. Chakinala et al.\textsuperscript{12} have reported the applicability of a combination of hydrodynamic cavitation and advanced Fenton process for treatment of industrial effluents. Pradhan and Gogate\textsuperscript{13} have studied removal of p-nitrophenol using venturi and orifice plate as cavitating device and Fenton chemistry. It was observed that extent of removal increased with an increase in inlet pressure. The extent of removal was higher for lower initial concentration of pollutant.

**Vortex diode as cavitating device**

In the present work, a new cavitating device developed recently by Ranade et al.\textsuperscript{11,14} in the form of vortex diode has been used for effluent treatment and other applications. The basic design of a vortex diode consists of cylindrical axial port, a tangential port and a chamber connecting the two ports. The chamber is characterized by its diameter and height, which decide the chamber volume. The flow entering the device through the tangential port sets up a vortex and establishes a large pressure drop across the device. Fig. 1 shows the principle of working in vortex diode. The hydrodynamic cavitation set-up used in the present study is shown in Fig. 2. The setup includes a holding tank of 60 L capacity, a multistage centrifugal pump of rating 2.2 kW (2900 RPM), three cavitation reactors e.g. Vortex diode, orifice, venturi and control valves. Flow/pressure transmitter and thermocouple were used for the respective measurements. The entire set-up is fabricated in SS-316.

![Vortex diode and schematic representation of cavity growth and collapse](image1)

**Fig. 1:** Vortex diode and schematic representation of cavity growth and collapse

![Hydrodynamic cavitation reactor setup](image2)

**Fig. 2:** Hydrodynamic cavitation reactor setup
RESULTS AND DISCUSSION
Adsorption in wastewater treatment-removal of phenols and acids
The surface area and properties of the adsorbents are listed in Table 1. The results on treatment of synthetic phenolic wastewaters using adsorbents have been given in Fig. 3.

It is evident that adsorption is highly effective in the removal of phenolics from wastewaters. The adsorbent, TAC shows maximum removal capacity for the phenol and 4-aminophenol and as high as 85% COD removal is observed. The results on various adsorbents are highly illustrative and following inferences can be drawn:
1. Though, all the adsorbents are carbon based, there is huge variation in the removal behaviour of phenol and 4-aminophenol among the 4 adsorbents selected.
2. Huge difference in the selectivity behaviour is observed for phenol and 4-amino phenol. While, adsorbent- Norit has ~70% removal for 4-aminophenol as against just ~10% for phenol, TAC has only slightly higher capacity for 4-aminophenol than phenol. The adsorbent GH2x has almost equal capacity for both 4-aminophenol and phenol, close to ~65% while SRCx has shown reverse selectivity-capacity for phenol more than that for 4-aminophenol as compared to all other adsorbents.
3. The results on removal of phenol and 4-aminophenol clearly highlight the differences in the surface properties of these adsorbents, thereby indicating strong physico-chemical nature of adsorption that is less dependent on the surface area of adsorbent.

Table 1 : Characterization of adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BET surface area (m².g⁻¹)</th>
<th>Total pore volume (cm³.g⁻¹)</th>
<th>Average pore diameter (nm)</th>
<th>Surface modification</th>
</tr>
</thead>
<tbody>
<tr>
<td>GH2x 4/6</td>
<td>1329</td>
<td>0.807</td>
<td>2.43</td>
<td>Impregnated with specialty chemicals</td>
</tr>
<tr>
<td>SRCx 4/6</td>
<td>1098</td>
<td>0.710</td>
<td>2.58</td>
<td>Impregnated with specialty chemicals</td>
</tr>
<tr>
<td>Norit</td>
<td>905.9</td>
<td>0.699</td>
<td>0.308</td>
<td>None</td>
</tr>
<tr>
<td>TAC 4/10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Impregnated with specialty chemicals</td>
</tr>
</tbody>
</table>

![Fig. 3: Adsorptive removal of phenol from wastewaters](image)

[Adsorbent loading= 2.5 %; Initial COD (ppm), Phenol=120; 4-Aminophenol = 112]
4. Adsorbents having high capacity for removal of both phenol and 4-amino phenol are most suitable for treatment of wastewaters to meet the limits of discharge. In this regard, TAC and GH2x can be best suited for removal of these from wastewaters.

5. Adsorbents such as Norit activated carbon can be best suited for separation of 4-amino phenol from phenol, as it has high selectivity for 4-amino phenol.

6. Overall, adsorption is highly effective in treating wastewaters containing phenolics.

7. Adsorbent selection is very important and critical to process viability. It is to be noted that most adsorbents reported in the literature based on carbon derived from lignite, rice husk, petroleum coke, porous clay etc. have exhibited capacity far less than 10 mg/g. A comparison of the results with the capacity reported in the literature\textsuperscript{15,16} shows that the adsorbents of this study have high capacity of adsorption even at low concentrations, indicating applicability in industrial wastewater treatment where low concentrations are invariably encountered. It was also observed that the selected adsorbents are highly effective for removal of acids. Fig.4 gives the results on removal of p-amino benzoic acid using different adsorbents. Norit Activated carbon showed maximum capacity with COD removal of ~83 %. The rest of the selected adsorbents viz., SRCx, GH2x and TAC are also fairly effective as they exhibit COD removal above 58 % (Fig. 4). Overall, it is seen that the judicious choice of adsorbent for specific organic contaminant is highly essential in efficient removal of harmful organic contaminants like phenol, substituted phenols and aromatic acids. It is also observed that the performance of the four adsorbents gets enhanced in presence of NH\textsubscript{2} group, showing the effect of the substituent nature. It may be inferred that the active sites in GH2x, Norit and TAC have more affinity for binding with this group as seen from the COD removal capacity of the adsorbents for 4-aminophenol and 4-aminobenzoic acid.

![Fig. 4](https://example.com/f4.png)  
\textbf{Fig. 4 :} Adsorptive removal of acid from wastewater

\textbf{Cavitation in wastewater treatment - removal of phenols}  
The cavitation number (Cv), characterizing cavitation is defined as

\[ C_v = \frac{p_d - p_v}{0.5 \rho v^2} \]

where \( p_d \) is downstream pressure, \( p_v \) is vapor pressure, \( \rho \) is density and \( v \) is velocity of the fluid. Typically, cavities are generated at a condition \( C_v \leq 1 \), however, cavities are known to get generated at a value of \( C_v > 1 \) due to the presence of some dissolved gases/ suspended particles that provide additional nuclei for the cavities to form. As the pressure increases, velocity at the throat of cavitating device increases, which subsequently reduces the cavitation number. Hence, higher degradation
can be obtained at lower cavitation number. However, at substantially high flow rates, cavities can start coalescing to form a larger cavitational bubble (cavity cloud), subsequently resulting into an incomplete collapse, thereby reducing the cavitational yield/ degradation rate after the optimum is reached. In the present study, different inlet pressure conditions were screened for obtaining $C_v$ for optimum cavitation conditions. It was observed that degradation of phenols using cavitation is very difficult. While, positive results were obtained on degradation of phenol, the degradation of 4-amino phenol was found to be practically negligible under the conditions of this work-for both vortex diode as well as for orifice. The results of phenol degradation are shown in Fig. 5. Two different pressure drop conditions have been studied, 0.5 and 2 kg/cm$^2$ in vortex diode and 2.0 and 5.0 kg/cm$^2$ for orifice. It was observed that for initial COD of 105 mg/L, only vortex diode yields appreciable degradation of phenol of the order of 15%, for pressure drop of 0.5, while the hydrodynamic cavitation using orifice showed practically no degradation of phenol, even at high pressures.

The reason for the discrepancy in the degradation of p-amino phenol and phenol can be attributed to the oxidation reaction behaviour of these two molecules. It is felt that the role of physical destruction of molecules in this particular system is rather negligible in cavitation and degradation can be attributed to the reaction of generated hydroxyl radicles / hydrogen peroxide with the phenols. This needs further detailed investigation. The difference in performance clearly underlines the importance of reactor configuration in hydrodynamic cavitation. Further, the experimental results in vortex diode and orifice indicate difference in the mechanism of cavity formation, growth and collapse. It is also evident that energy utilization in the case of vortex diode is substantially less than that in orifice due to lower pressures. It is clear that phenol is comparatively difficult to degrade physico-chemically and hence destructive method of cavitation is less attractive as compared to adsorption, where recovery / separation of chemicals is also possible. However, since concentration and inlet pressure both have significant impact on the cavitation performance, it is felt that hydrodynamic cavitation using vortex diode can be suitably combined with adsorption process to bring down the pollutant levels to meet prescribed limits. There is, however, need to study the effects of various parameters in detail, especially on cavitation to determine techno-economical viability of the process, in isolation or in combination.

**CONCLUSION**

Adsorption is found to be highly effective in the removal of refractory pollutants such as phenol, p-amino phenol and p-amino benzoic acid. The selection of adsorbent is important and surface modification plays crucial role in the removal of organic acids. A relatively new technology of hydrodynamic cavitation also has potential in the wastewater treatment through...
mineralization of pollutants. Further, hydrodynamic cavitation using newer forms of devices such as vortex diode appears to be more promising as compared to conventional devices such as orifice and venturi. A process integration approach using adsorption for recovery/removal of chemicals and cavitation for attaining desired levels of COD reduction through mineralization can be promising for industrial wastewater treatment.

REFERENCES


