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Treatment of pharmaceutical wastewater from cephalosporin processing unit

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Abstract

Wastewater generated from Cephalosporin processing unit is very hard to degrade directly through biological process, and could cause great harm to the environment and human being if disposed untreated. This study has been carried out to develop an efficient treatment process of Cephalosporin processing unit wastewater through chemical, biological and physicochemical processes. It has been found thatbefore conducting biological treatment, theantibacterial activity of antibiotics has to be disabled through inactivation of β-lactam ring by pH adjustment (raising pH to around 10.5). Simple aeration processwithout any adjustment of pH and without addition of any nutrient achieved 62%COD reduction. Finally chlorination process followed by pressure sand filtration and activated carbon adsorption process achieved further reduction of COD and BOD_5satisfying the national discharge standards. Activated carbon adsorption process also significantly reduced residual chlorine concentrationin the effluent. BOD_5, COD and residual chlorine concentrations of raw wastewater and effluent have been measured as indicatorof treatment efficiency. Optimum aeration period and optimum chlorine dose have been determined through extensive laboratory experiments. Optimumflow rate and contact time for activated carbon filtration hasalso been determined.

Keywords: Wastewater from cephalosporin production, β-lactam ring breakdown, Activated Carbon Filter

1. Introduction

During the last one decade remarkable development has taken place in the field of textile and pharmaceutical industries and large numbers of these industries have been established mostly around Dhaka city.Wastewater generated from cephalosporin production processes contains organic substances, soluble andcolloid solid substances at high concentrations. It also contains non-biodegradable toxic substances and bacteriostatic antibiotics. Untreated and partially treated pharmaceutical liquid wastes discharged into water courses degrade the water quality and environment severely. Thus it threatens the ecosystem and livelihood of people who use these sources of water. Therefore, treatment of such wastewater is necessary for the

protection of environment and public health. The Department of Environment (DOE) has completely prohibited the disposal of such wastewater in the environment. Selection of appropriate treatment option is one of the major steps towards reducing pollutants from effluents of pharmaceutical industries. In this study, an attempt has been made to provide a guideline for designing and operating treatment plant for pharmaceutical liquid waste. Different treatment options have been assessed to develop efficient and cost-effective treatment option which will encourage the industries to install and run effluent treatment plant.

2. Methodology

The quality of pharmaceutical wastewater varies greatly in composition depending on the type of medicine produced, and the type of antibiotics present. In this study, wastewater samples were collected from Aristopharma Ltd. The state-of-the-art Aristopharma's plant, located at Shampur-Kadamtali I/A, 10 km from central Dhaka, is equipped with highly sophisticated and advanced facilities.Wastewater sampleswere collected over a period of nine months from May 2013 to January 2014. The samples collected were promptly transported to the laboratory for detail characterization and batch experiments. A total of 13 batches of experiment have been run in the laboratory to develop the design criteria and selection of an optimum unit processes. For simulating effect of filtration through activated carbon, a1.75 in diameter PVC pipe was used as the activated carbon filter column. The depth of activated carbon in the filter column was 9 inches. At firsts, pH, EC, color, turbidity and COD are measured of raw sample. Raw wastewater sample adjusted with pH 10 then added to sludge (different sludge volume is taken to show the variation of result). A batch consists of six beakers (1000ml) each with 500 ml sample is taken for experiment. The aeration is done by diffuser. After certain period of time, diffuser is turned off and sample is collected after 30 min settling time.

In this study, COD of the sampleswere measured using Closed Reflux-colorimetric Method'' (SM 5220D).“Respirometric Method” (SM5210 D) using OxiTop control (OxiTopR OC 100) and BOD incubator was been used to determine BOD.All other parameters were measured using Standard Methods.

3. Model Studies and Results

Table 1
Characteristics of raw wastewater samples from the Cephalosporin processing unit

Wastewater Quality Parameter	Concentration Range Present		Average Conc.	Discharge Standard (ECR, 1997)
	Minimum Value	Maximum Value		
Turbidity (NTU)	32	652	131	----
Color (Pt-Co unit)	40	810	268	----
Electric Conductivity(µS /cm)	380	2350	1096	≤1200
pH value	6	8.86	7.08	6-9
Chemical Oxygen Demand (mg/l)	245	959	625	≤200
Biochemical Oxygen Demand (mg/l)	81	316.5	206	≤50

Laboratory scale model studies have been conducted to determine the design criteria and for the selection of appropriate treatment unit processes for treatment of wastewater of a Pharmaceutical industry particularly from cephalosporin processing unit. In order to ascertain the treatability of pharmaceutical liquid wastewater, the wastewater quality parameters

including pH, color, and turbidity values, BOD, COD, and suspended solids concentrations have been measured at different stages during model studies. Table 1 shows the characteristics of wastewater sample from Cephalosporin processing unit.

3.1 Initialization and Preparation for Biological Process

3.1.1 pH adjustment and Nutrient addition

Initially three weeks of continuous aeration showed no changes in the quality of raw wastewater even in the presence of nutrients. Therefore, it was understood that biological process is not feasible without inactivation of antibiotic property of Cephalosporin[2]. Both pH increase and decrease showed good result in inactivation of antibiotic property, however, increase of pH was much easier to achieve. Prior to diffused aeration process, pH of raw wastewater samples were increased to around 10.5to breakdown the β-lactam ring of Cephalosporin through alkaline hydrolysis of β-lactam ring (nucleophilic attack on the β-lactam carbonyl group) causing inactivation of un-biodegradable antibiotics[5]. An alkaline solution (20mg/l caustic soda) was mixed carefully with the wastewater and the mixture was allowed to equilibratefor 90 minutes for completion of chemical reaction. pH value gradually reduced to about 8 to 8.5 due to the formation of CO_2 due to biological oxidation of organic matters during aeration process. Prior to aeration process for biological oxidation of organic matter Di-ammonium phosphate (DAP) was also mixed with the wastewater sample as a source of nutrients (in a ration BOD: N: P equals 100:5:1) to promote suitable environment for microbial activity.

3.1.2 Direct Aeration without Seeding

Initially pre-aeration for 24 hours wasdone to obtain a homogenous mixture of wastewater sample without any seeding. Nearly 22% removal of raw COD was achieved through this process possibly due to the removal of Volatile Organic matters (VOC).

3.1.3 Addition of Sanitary Sewage

Addition of at least 20% domestic sewagewas done for dilution of raw sewage and to ensure adequate micro-organisms in the mixture.

3.2 Acclimation for Biological Process and Variation of Aeration Period

3.2.1 Effect of Mixed Sludge (Bio-mass) Volume

To achieve a reasonable initial MLSS concentration around 3000-3500 mg/l and to maintain an initial food to microorganism ratio in the range of 0.10 to 0.4, different volumes of settled sludge was mixedwith wastewater sample. The settled sludge was kept in suspension through diffusers for effective contact (suspended growth) amongmicroorganisms and organic (substrate) matter.

3.2.2 Aeration Rate

Oxygen requirement calculation for biological process has been done considering average influent and effluent BOD_5 as 806 mg/l and 40 mg/l, respectively. Therefore from mass balance equation, the required oxygen demand would be 11.49 kg of O_2/hr and the required air flow should be 54.71 m^3 of air/hr (considering weight of air 1.2 kg/m^3). Supplied air flow rate should be 4.22 m^3/minute(considering SOTE around 18%).

3.2.3 Variation of Aeration Period with Increased Experimental Batch Number

At the beginning of the biological aeration process (i.e. for the first batch experiment),it took around 48 hours for the acclimation of microorganisms.However, with the passage of time (subsequent batch experiments) acclimation of microorganism with the pharmaceutical samples became more effective and as a result the oxidation rate enhanced significantly and COD value reduced at a faster rate with aeration period [10]. Every time seeding was done through settled sludge obtained from previously aerated wastewater samples. In the 7th and 8th batches of experiment, residual COD value reduced down below the National Discharge Standard (ECR, 1997) of 200mg/l within 8 hours aeration period as shown in Figure 1. Therefore 8-9 hours aeration period in the aeration tank could be considered optimum to achieve the desired limit for COD as per National Discharge Standard (ECR, 1997) provided that all above mentioned environmental conditions are satisfied. The desired BOD_5 as per National Discharge Standard (ECR, 1997) is 50 mg/l. However, this limit could not be achieved during this 8-9 hours aeration period indicating that tertiary treatment would be required.

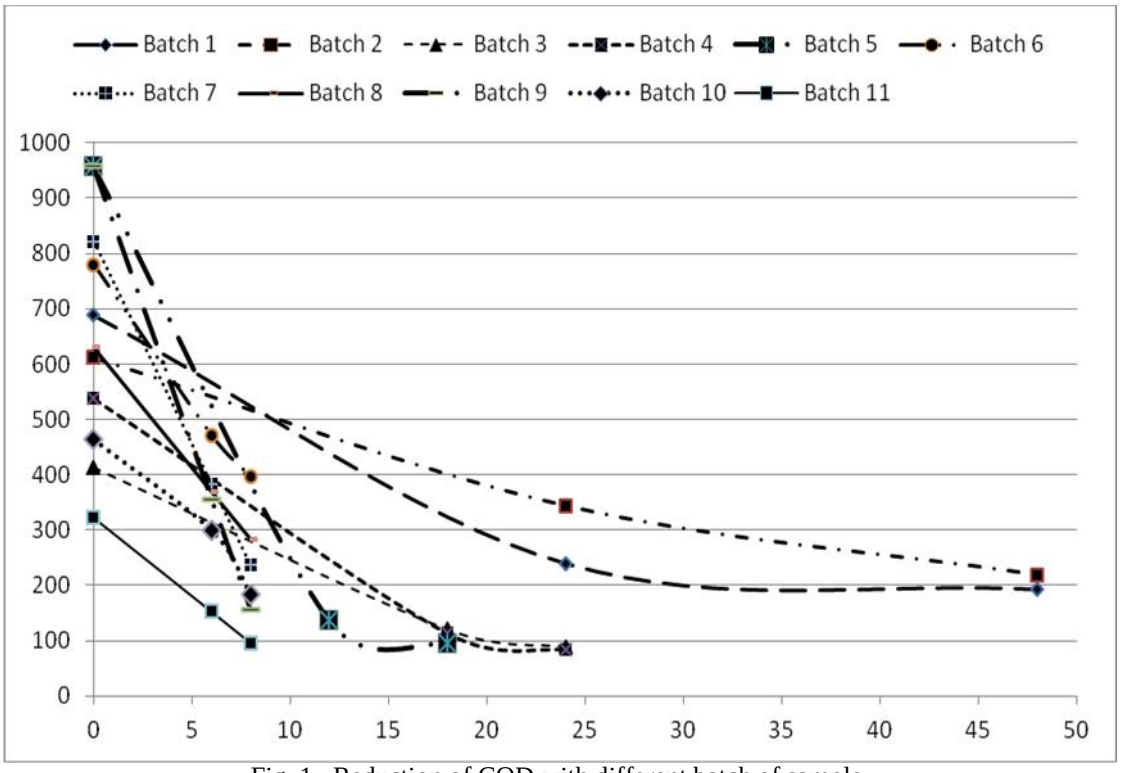

Fig. 1. Reduction of COD with different batch of sample

3.2.4 Disruption of Biological Process with Change of Wastewater Quality

When fresh mixed (from different unit of pharmaceutical industry) pharmaceutical wastewater sample with high COD values were added to the batch samples (i.e. mixture of pharmaceutical wastewater and sewage)undergoing aeration process, it caused complete disruption of the biological process (i.e. biodegradation). To overcome the problem, sanitary sewage and sludge were again added with Cephalosporin unit wastewater. After aeration for a couple of weeks again for the acclimation process, the growths of fresh healthy bio-flocs were observed. Therefore, it may be suggested that wastewater from other Pharmaceutical units should be treated separately or should be diluted to reduce the organic strength[6].

3.3 Effect of Tertiary Treatment Process on COD Reduction

3.3.1 Chlorination of Aerated Effluent

Chlorination of biologically treated effluent from Cephalosporin unit is a must for complete disinfection before disposal in the environment. The effect of chlorination on COD reduction have also been determined and laboratory investigation results reveal that a chlorine dose around 20 mg/l and mixing time of one hour to beadequate to achieve the desired results.

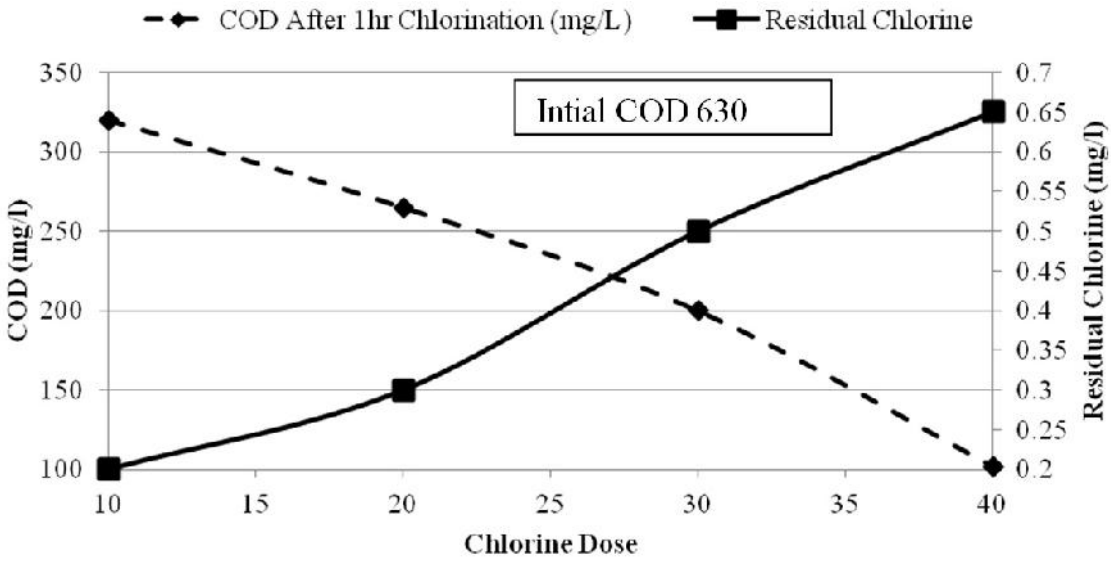

Fig. 2. Effect of Chlorine on Raw Wastewater

3.3.2 Activated Carbon Filtration after Chlorination

To bring down the residual chlorine concentration within the reasonable limit of 0.2 to 0.3 mg/l before disposal in the environment, Granular Sand Filtration (filtration rate 10 m/h) process followed by Activated Carbon Filtration process would be necessary. Chlorination process involves for 30 min & presence of chlorine dose facilitates the reduction of COD up to 80% whereas aerated sample has a percentage of removal on average 65~70%. The analysis on three separate samples has been shown on the graph above. In the laboratory model investigation, residual chlorine concentration reduced down to almost zeroand complete disinfection of micro-organisms achieved after activated carbon filtration process.

4. Selection of Unit Operation/Processes and Determination of Design Criteria

At the beginning of the treatment processes, Screen should be provided as a safeguard to machineries, pumps, diffusers etc. from any possible large suspended and floating materials. Since presence of fine suspended solids in pharmaceutical wastewater sample is insignificant, *Primary clarifier* would not be required for settling of suspended solids. Alkaline solution (lime/caustic soda) should be added and mixed in the *Inlet chamber*to increase pH value above 10.5. Air should be supplied continuously inthe *Equalization Tank* for homogenous mixing of incoming wastewater and to keep wastewater with all solids in suspension. “Sequential Batch Process” has been proposed for its simplicity in operation and process control. Moreover, aeration and clarification could be done in the same chamber which will significantly minimize the construction cost. It has already been observed that aeration period

of around 8 hour in the *Aeration tank* excluding 24 hours pre-aeration in the equalization tanks would be sufficient enough to achieve the desired COD level of 200 mg/l.

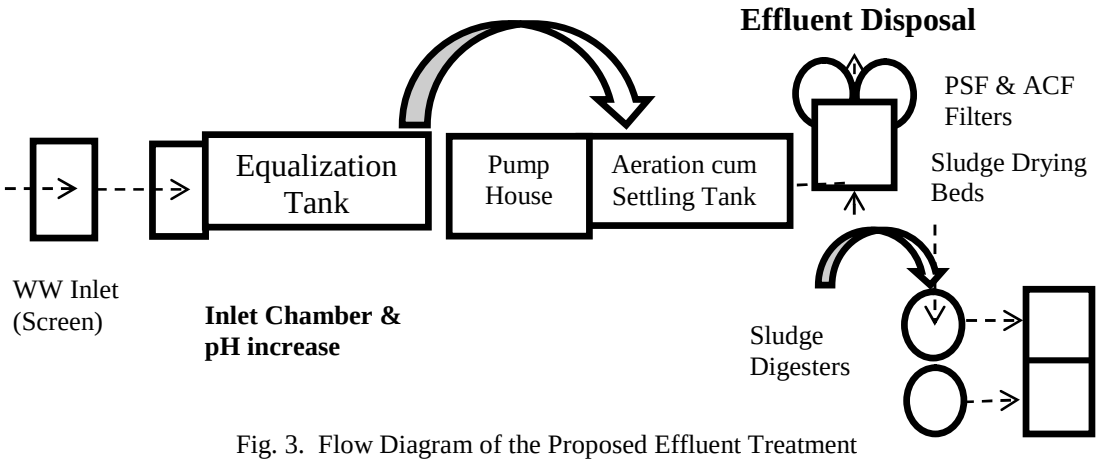

Fig. 3. Flow Diagram of the Proposed Effluent Treatment

Actual detention time in the aeration tank would be = 1.0 hours wastewater transfer time from equalization tank to aeration tank + 8.0 hours aeration period + 1.35 hours settling (0.75 plain settling + 0.6 hour settling and drain out from top outlet) + 0.65 hour drain out from bottom outlet = 11 hours. Therefore, each day two batches of aeration of wastewater sample could be performed within 24 hours period.

Settled effluent should be chlorinated with 20mg/l Cl_2 dose and mixing period ofone hour in a *Chlorine Contact Chamber* (CCC) to oxidize residual organic matter and for complete disinfection. Finally *Granular Sand Filters* followed by *Activated Carbon Filters* would serve as a polisher of the treated effluent and also for de-chlorination purpose. The overall reduction of the pollutant concentration is shown in Table 2.

Table 2
Reduction of Pollutant in Different Stages of Treatment

Wastewater Quality Parameter	Raw / Influent Sewage	Post Biological Treatment	After Chemical Treatment (Cl_2 = 20mg/l)	After PCF and Activated Carbon Filtration	Discharge Standard (E.C.R, 1997)
COD (mg/l)	959	155	109	21	≤200
EC (µS/cm)	592	1147	840	732	≤1200
Color (Pt-Co unit)	100	78	62	33	≤200
pH	10.32	8.98	7.52	7.3	6-9

Post-Aeration Chamber would operate for a short period of time (around 10 minutes) to increase dissolved oxygen level. This process would be required to ensure the desire minimum DO level of 4.5 mg/l in the final treated effluent.

DOE has ruled that, effluent from pharmaceutical cannot be disposed outside. Tertiary treated effluent would be collected in a disposal pond for aquaculture and could also be used for washing and gardening purpose. Ground water recharge is an alternative option of reuse of treated effluent. This disposal and reuse would ensure zero flow effluent from the proposed pharmaceutical processing plants [1].

5. Conclusion

Because of the potential health risks associated with cross-reactivity (cross-sensitivity) of beta-lactams, pharmaceutical manufacturers should assess and establish stringent controls (including appropriate facility design provisions assuring separation) to prevent cross-contamination with effluent from cephalosporin processing unit. It is expected that if wastewater from Cephalosporin processing Pharmaceuticals units is treated properly in anETP,which has been designed carefully on the basis of laboratory scale model study results and is operated properly and maintained carefully,pollution of surrounding environment could be avoided and desired effluent discharge limitcould be attained.Although chemical treatments are suitable to reduce color, COD, nitrate, phosphate and many other heavy metals, but such treatments increase TDS and EC of the effluent. As biological process is economic, effective and less energy consuming; combination of biological and subsequent chemical process is much more effective and less time consuming due to the low rate of degradation of organic matter with time.Regular monitoring of effluent quality should be performed through establishing an onsite environmental monitoring laboratory with required apparatus and equipment.

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