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Research Paper

CHEMOAUTOTROPHIC ACTIVATED CARBON OXIDATION: AN ADVANCED OXIDATION PROCESS FOR THE REDUCTION OF SULPHATE IN PHARMACEUTICAL EFFLUENT

Geeta Chittala[1*], G Sekaran[2], Paul S Mogadati[1] and M Anjireddy[3]

Corresponding Author:* ***Geeta Chittala,* ✉ *geetachittala@gmail.com*

In general, industrial wastewaters contain suspended, colloidal and dissolved (mineral and organic) solids. In addition, they are either excessively acidic or alkaline in nature and they may contain high or low concentrations of chromophoretic compounds. These wastes may contain inert, organic or toxic materials and possibly pathogenic bacteria. These wastes may be discharged into the sewer system provided they have no adverse effect on treatment efficiency or undesirable effects on the sewer system. It may be necessary to pre-treat the wastes prior to release to the municipal system or it is necessary to a fully treatment when the wastes will be discharged directly to surface or ground waters. Industrial wastewaters are effluents that result from human activities which are associated with raw-material processing and manufacturing. Pilot plant studies were conducted to determine the sulphates removal efficiency in pharmaceutical wastewater using Chemo autotrophic activated carbon oxidation technology and were observed to give satisfactory results.

Keywords: Chemoautotrophic activated carbon oxidation technology, Wastewater, Bacteria, Sulphate

INTRODUCTION

The wastewater treatment aims mainly at the removal of contaminants like suspended solids, biodegradable organic matter, pathogens, nutrients, refractory solids, heavy metals, dissolved inorganic solids etc. Wastewater can be treated with different methods which involve primary treatment, biological treatment, tertiary or advanced treatment. In the primary treatment, the physical forces will play an important role in removing certain types of pollutants, the biological treatment of wastewater is commonly referred to it is very similar in concept to the natural biodegradation of organic matter and tertiary treatment deals with treatment of chemicals.

[1] Dr. Reddy's Laboratories Ltd., Hyderabad.
[2] Environmental Technology Division, Central Leather Research Institute (CLRI) (CSIR), Adyar, Chennai.
[3] JNTU, Hyderabad.

PHARMACEUTICAL INDUSTRIES EFFLUENT CHARACTERISTICS AND NEED FOR SULPHATES REDUCTION IN WASTEWATER

TThe pharmaceuticals manufacturing industry encompasses the manufacturing, extraction, processing, purification and packing of chemical to be used as medication. Most of the active ingredients marketed and sold as drugs are manufactured by chemical synthesis. The wastewater generated from pharmaceutical industries contains a variety of pollutants that include aromatic, aliphatic spent chemicals, solvents and other inorganic pollutants.

The pharmaceutical industries discharge a considerable concentration of Sulphate ions in soluble form besides organic chemicals. Many sulphate compounds are readily soluble in water.

The conventional aerobic biological wastewater treatment options have very poor efficiency to remove sulphate the wastewater. Hence, there has been continuous research to eliminate sulphate from the wastewater. The focal theme of the present investigation is to use the immobilized Bacilus sp. for the treatment of pharmaceutical wastewater containing sulphates.

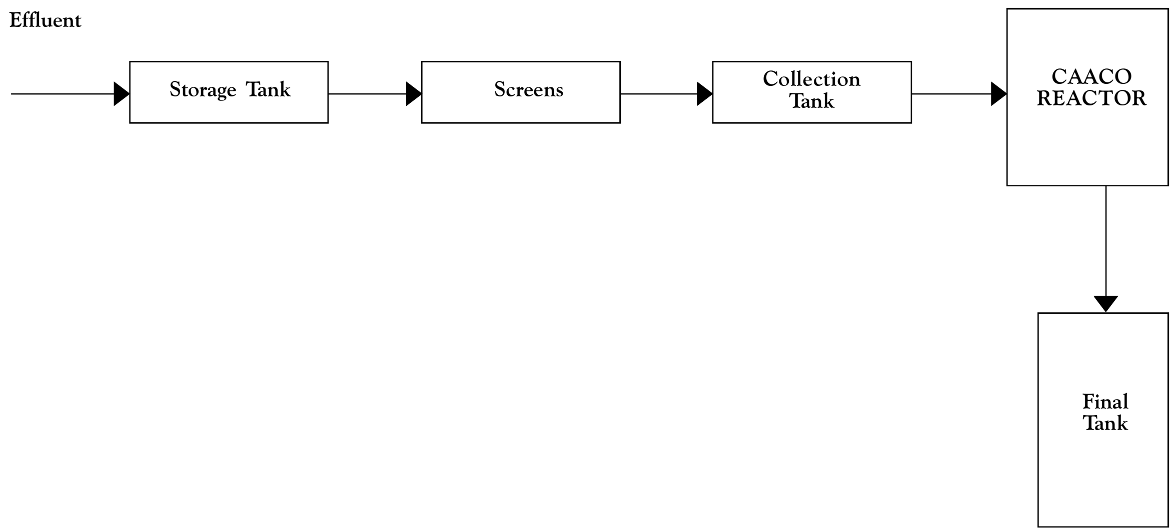
EXPERIMENTAL SET UP

The bench scale unit used in the present investigation is the prototype of ETP. The laboratory scale experimental model of ETP to treat a flow of wastewater 5litres/day is presented in the schematic flow diagram. The parameters were monitored to assess the performance of the laboratory model.

The laboratory model comprised of the following:

1. Storage tank
2. Screens
3. Collection tank
4. CAACO reactor
5. Final Tank

FLOW DIAGRAM FOR PILOT PLANT



DESCRIPTION OF EACH UNIT OF PILOT PLANT

Storage Tank

The storage tank is of dimensions 0.6 mtrs in Depth, 0.3 mtrs in Length and 0.3 mtrs in Breadth. The effluent is collected from the existing ETP, effluent was autoclave at 122 degree Celsius temperature and at 15 psi above atmospheric pressure to destroy any viruses present in the wastewater, and the sterile effluent of volume about 5liters was stored in the storage tank.

Screens

The wastewater from the storage tank was passed through the screens to remove the floating and coarse solids.

Collection Tank

The screened effluent was collected in the collection tank of dimensions of 12.7 cms in Depth, 0.3 mtrs in Length and 0.6 mtrs in Breadth. The screened effluent was collected in the collection tank.

CAACO Rector

The CAACO reactor dimensions are 8 inches Diameter and 9 inches height. The reactor has a layer of pebbles, CAACO media and has diffused aeration system. The overflow from the collection tank flows into the CAACO reactor were 2 hrs detention time is provided.

Chemo Autotrophic Activated Carbon Oxidation (CAACO) Reactor: The reactor used in this study had a total volume of 720 ml and working volume of 356 ml, with dimensions of 5.5 cm diameter and height of 30 cm. It consisted of 2.5 cm layer of gravel (5mm) separated by a 2.5cm layer of gravel (3 mm). This was followed by a 10 cm layer of coarse sand (1mm). A 2.5 cm void space was left at the base to facilitate collection of the filtered water. The collection system consisted of header and laterals. The header was of diameter 10mm and laterals of diameter 5mm. The laterals were perforated with 0.8mm diameter holes. The reactor was filled with mesoporous activated carbon immobilized with *Bacillus sp.* isolated from a facultative lagoon to a bed height of 15 cm. Based on the recipe used for cell immobilization described above, the initial biomass concentration was 1.87g/L of reactive (void) volume. The sizes of carrier particles and bioreactors used in this study were arbitrarily chosen for ease of observation. The oxygen required for the oxidation of organics in wastewater was supplied in the form of air at a pressure of 0.6 kg/cm^2 through an air diffuser placed in the carbon bed. The sand filtered sewage was distributed onto the surface of the carbon bed via a PVC pipe (10mm) perforated with 0.8mm diameter holes. The sand filtered sewage was fed to the PVC distributor using a peristaltic pump (Watson Marlow). The temperature was maintained at 30±1^{o}C in order to minimize the change in water quality by temperature fluctuation. Treated sewage was drained from the base of the filter through a 10mm wide slit which was open to atmosphere. The immobilized cell reactor was cleansed by pumping at least two void volumes of sand filtered waters before each sewage sample was tested. One void volume of treated wastewater was discarded during test run.

Final Tank

The final tank is of 5 inches Depth, 5 inches Length and 5 inches Breadth. The treated water is collected in the final tank.

Design Criteria

1. Flow Rate: The flow rate was regulated to 4 liters per hour using peristaltic pump.
2. Detention period: Detention period of 2 hours was provided to the CAACO rector for the degradation of organic compounds.
3. CAACO Reactor: In the CAACO system the wastewater was distributed through the special distribution system into the reactor. The organics contained in the wastewater when flows down the reactor through the mesoporous activated carbon (characteristics of mesoporous activated carbon provided in Table 1), the immobilized microorganisms perform biological degradation of the organics and the media performs catalytic oxidation at the same time. The media is held between the strainer plates. Air from an air blower was distributed in the space between the CAACO media and the sand gravel media.

Table 1: Characteristics of Rice Bran Based Activated Carbon

S. No.	Parameters	Values
1.	Carbon (%)	48.45
2.	Hydrogen (%)	0.7
3.	Nitrogen (%)	0.1
4.	Ash Content(%)	42.61
5.	Bulk density (g/ml)	0.405
6.	Moisture content (%)	3.8
7.	Ash content (% by mass)	40
8.	Matter soluble in water (%)	0.428
9.	Matter soluble in acid (%)	3.908
10.	pH	6.66
11.	Decolorizing Power (mg/g)	52
12.	Phenol number (mg/g)	3.18
13.	Ion Exchange Capacity (meq/g)	0.015
14.	Surface Area (BET), m^2/g	420

MATERIALS AND METHODS

The Wastewater was analyzed before and after treatment and the analyzed parameters were COD, BOD and Sulphates (Table 2). The dissolved organics estimated as COD and BOD has been proved to be decreased to a credible level such that the treated wastewater can be discharged into open land. The treated wastewater has been used for irrigation and it has recorded the growth of vegetative plants, commercial crops and ornamental plants.

Table 2: Analysis of Effluent for COD Before and After CAACO Treatment

Days	COD (mg/lit)		BOD (mg/lit)	
	Inlet	Outlet	Inlet	Outlet
Day 1	240	90	350	30
Day 5	220	120	260	45
Day 10	350	90	350	32
Day 15	500	100	345	46
Day 20	280	65	387	56
Day 25	287	80	245	45
Day 30	398	198	265	56
Day 35	265	70	378	48
Day 40	276	87	348	47
Day 45	342	165	234	48
Day 50	276	70	420	42
Day 55	312	65	276	40
Day 60	265	123	298	42
Day 65	287	120	235	43
Day 70	234	150	450	37

Sulphates were analyzed by UV Spectrophotometer (Table 3). Ultraviolet-visible spectrophotometer: Ultraviolet-visible spectrophotometer refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption or reflectance in

Table 3: Table 3: Analysis of Effluent for Sulphates Concentration in Inlet and Outlet of Pilot Plant

Days	Inlet Sample mg/lt	Outlet Sample mg/lt
Day1	3750	1936
Day 2	3750	1674
Day3	3750	1873
Day4	3750	1651
Day5	3750	1234
Day6	3750	1983
Day7	3750	1987
Day8	3750	1998
Day9	3750	1765
Day10	3750	1176
Day11	3750	2345
Day12	3750	1876
Day13	3750	1983
Day14	3750	1356
Day15	3750	1987
Day16	3750	1873
Day17	3750	1655
Day18	3750	1239
Day19	3750	1983
Day20	3750	1987
Day21	3750	2265
Day22	3750	1176
Day23	3750	1309
Day24	3750	1562
Day25	3750	1879
Day26	3750	1873
Day27	3750	2987
Day28	3750	1765
Day29	3750	1387
Day30	3750	1367

the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state. The absorbance for the pilot plant samples was noted at 420 nm. 30 gms of sodium sulphate was dissolved in 5 liters of effluent and the pilot plant was run as a batch process for one months period. Remarkable reduction efficiency of sulpahtes was observed.

TREATMENT SUMMARY

The waste water after passing through screen chamber will be collected in the Collection cum Equalization Tank (EQT). From collection tank, the effluent flows into the CAACO reactor were 2 hrs detention periods was provided .When the wastewater flows down the CAACO reactor through the specially developed catalyst based media, the immobilized microorganisms perform biological degradation of the organics and the media performs catalytic oxidation at the same time. Air is provided with the help of an Air Blower that provides the required oxygen to the facultative Microorganisms. From the CAACO reactor effluent passes to final tank. 30 gms of sodium sulphate quantity in 5 ltrs of effluent. From the final tank the samples were collected and analyzed COD, BOD and sulphates to know the efficiency of CAACO for sulphates reduction.

RESULTS AND DISCUSSION

1. The COD of inlet sample ranges from 220-500 mg/lt and COD of final tank range from 65

to 198 mg/lt. The efficiency of pilot plant to remove COD is 64% as shown in Table 2.

2. The BOD of inlet sample ranges from 350 - 387mg/lt and BOD of final tank ranges from 30- 56mg/ltrs. The efficiency of pilot plant to remove BOD is 86% as shown in Table 2.

3. The pilot plant was run as batch process for analysis of sulphates reduction, by using CAACO system 52 % reduction of sulphates was obsereved as shown in Table 3.

CONCLUSION

Pharmaceutical industries use considerable quantities of poorly biodegradable organics. The biodiversities employed in effluent treatment units are ineffective to remove organics in wastewater as the compounds themselves or their metabolites are toxic. The present study consists of anaerobic and aerobic bacteria in rice bran based activated carbon and air was supplied for the oxidation of organics in wastewater, thus the system was named Chemoautotrophic activated carbon oxidation (CAACO).The immobilized bacterial species and activated carbon were quite successful in removing the organics in wastewater at low detention period of 2h. The efficiency of treatment of pharmaceutical wastewater is good with CAACO media. There is about 64% efficiency observed with CAACO media for reduction of sulphates. Thus the resin of the CAACO reactor is more efficient in reduction of sulphates than the conventional methods. In this study a simple, fast and reliable UV spectrophotometric method was used for the determination of sulphate concentration and in turn the values helped to know the reduction efficiency by CAACO.

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