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REDUCTION OF CHEMICAL AND BIOCHEMICAL OXYGEN DEMAND AFTER TREATMENT OF PHARMACEUTICAL EFFLUENTS

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ABSTRACT

Pharmaceutical effluents are disrupting the environment and it is important to utilize such effluents for good purpose. Therefore, the present study is undertaken to treat effluents using calcium oxide and ferrous sulfate, wherein calcium oxide produces calcium hydroxide resulting basic pH, which is neutralized by ferrous sulfate. This treatment reduced the chemical oxygen demand (COD) and biochemical oxygen demand (BOD) to almost 98-99%. The effluent reacted with calcium hydroxide and oxidized ferrous into ferric hydroxide (precipitates). By this treatment, maximum solids were settled down in the form of sludge. The resulting neutralized wastewater may be used for agriculture and irrigation purpose. This process is very easy and effective in the improvement of water quality from pharmaceutical effluents.

Keywords: Chemical oxygen demand, Biochemical oxygen demand, Calcium oxide, Ferrous sulfate, Pharmaceutical effluents

INTRODUCTION

All the pharmaceutical and biopharmaceutical industries produce large amount of organic material and antimicrobials in their wastewater so it is important to treat the effluents to meet the Central Environmental Authority's discharge standards. Chemical oxygen demand (COD) is defined as the quantity/of a specified oxidant that reacts with a sample under controlled conditions. The biochemical oxygen demand (BOD) is an empirical test used to determine the relative oxygen requirements of the wastewaters, effluents and polluted waters. Bacterial growth requires nutrients such as nitrogen, phosphorus, and trace metals, these are added to the dilution water, which is buffered to ensure that the pH of the incubation is too long for practical purpose; therefore, 5 days has been accepted as the standard incubation period. Pilot-plant operations conducted at pharmaceutical manufacturing facilities can include biological studies, chemical research, and product development activities. Wastewater from pilot-plant operations conducted in conjunction with and related to existing pharmaceutical manufacturing operations is covered by this rule because these pilot-plant operations would most likely to generate wastewater with characteristics similar to the commercial manufacturing operations.

Each type of manufacturing operations in the pharmaceutical manufacturing industry is distinct. Fermentation and chemical synthesis manufacturing operations are typically largest scale batch processes characterized by large flow and relatively high BOD, COD and TSS concentrations. Biological extractions, mixing, compounding and formulation operations are characterized by low wastewater flows and relatively low BOD, COD and TSS concentrate. The literature review indicated that the treatment of pharmaceutical wastewater by the biological contact oxidation process and as a result the removal

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of COD, BOD, and color were >71, 97 and 30-40%, respectively. Moreover, the volumetric loadings of COD and BOO were 1.97 and 0.96 kg/m^3 day, respectively (Yuii *et al*., 1998; Massimo, 1989). Bio-decomposition of synthetic detergents and their adsorption on activated carbon was investigated in laundry wastewater (Agustina *et al*., 2014). Several physical and chemical methods such as stripping, adsorption, extraction and ion-exchange were used for water treatment (EPA, 1977). Use of Glauber's salt (agent 1227) resulted in a wastewater having COD <700 mg/L and BOD/COD ratio ˜0.5, which could easily be a biochemical method to meet the discharge standards (Sengupta, 2007). Sewage effluent containing COD was fed into an anaerobic treatment tank for 4 h and passed through a filter bed for removing COD (Jafari *et al.*, 2013). A mathematical model of oxygen demand (mass transfer) in settling tanks during the treatment of waste waters or water purification was also found in the literature (Gouveiam and Pinto, 2000). A two phase up-flow anaerobic digester operated under mesophilic conditions had a COD removal efficiency of 77-80% from wastewater from ethyl alcohol manufactured by fermentation of sugar syrup (Satyawali and Balakrishnan, 2008). The reduction of BOD and COD means the effluent is at acceptable level and will contribute the least side effect on the environment. It is possible only when its treatment is done for the reduction of chemical and biochemical oxygen demand according to the National Environmental Quality Standards (NEQS). A number of experiments were performed for the reduction of COD and BOD by the treatment with lime and ferrous sulfate, which gives very positive results. This study will provide the better environment as well as guideline for the future research.

MATERIALS AND METHODS

Chemicals and reagents

The materials used in the present study incuded calcium oxide, sulphuric acid, sodium thiosulfate, mercury sulfate, potassium dichromate, ferrous ammonium sulfate, ferroin, ferric chloride, calcium chloride and magnesium sulphate.

Methods

One liter effluent was taken in 2000 mL beaker and the pH was determined between 4.0 to 5.0. 12.0 grams of calcium oxide was added, during stirring, to attain the pH of experimental solution between 7.0 to 8.0. The stirring was continued for 2.0 h. After that the pH was determined that was in the range 7.0 to 8.0. The 8.0 grams of ferrous sulfate was added to attain the pH of experimental solution in between 6.5 to 7.5. The stirring was continued for 1.0 h. After the completion of 1.0 h stirring, noted the pH that was in between 6.50 to 7.0. Then, stirring was stopped to settle the treated effluent for 12.0 h. After the settling, sludge was formed. The sample from the sludge was decanted and kept for the determination of pH, COD and BOD.

Determination of COD

Preparation of blank solutions

Ten milliliters of deionized water was taken in 300 ml of quick fit flask and 0.2 grams of mercury sulfate ($HgSO_4$) was added followed by 5.0 mL of 0.25N potassium dichromate ($K_2Cr_2O_7$). Then, 15.0 mL of sulphuric acid (H_2SO_4) was added and refluxed for 2.0 h. Afterwards, the solution was cooled titrated against standardized 0.0625N ferrous ammonium sulfate (FAS) solution using ferroin solution as an indicator until the color was changed sharply from blue green to orange green.

Standard preparation

Thirty milliliters of deionized water was taken in 300 mL of quick fit flask and 5.0 mL of 0.25N potassium dichromate ($K_2Cr_2O_7$) and 15.0 mL of sulphuric acid (H_2SO_4) were added, and the solution was titrated against standardized 0.0625N of ferrous ammonium sulfate (FAS) solution using ferroin solution as an indicator until the color was changed sharply from blue green to orange green.

Sample preparation

Sample (0.1 mL) was taken and was diluted to 500 mL adding deionized water.

Procedure

One milliliter of diluted sample was taken in the 300 ml of quick fit flask and 9.0 ml of de ionized water was added. Then, 0.2 g of mercury sulfate ($HgSO_4$) was added followed by 5.0 mL of 0.25N potassium dichromate ($K_2Cr_2O_7$). Finally, 15.0 ml of sulphuric acid (H_2SO_4) refluxed for 2.0 h. The refluxed solution was cooled and after 2.0 h titrated against standardized 0.0625N ferrous ammonium sulfate (FAS) solution using ferroin solution as an indicator until the color was changed sharply from blue green to orange green. The COD was calculated using the following equation:

$$\mathrm{COD}\ (\mathrm{mg\ O2/L} = (\mathrm{A} - \mathrm{B})\ * \mathrm{M} * 8000\ /\ \mathrm{mL\ sample}$$

Where A is mL FAS used for blank, B mL FAS used for sample, M molarity of FAS and 8000 miliequivalent weight of oxygen x 1000 ml/L.

Determination of BOD

Distilled water (1.2 L) was taken in a reagent bottle, each bottle was treated with 1 mg/L of $FeCl_3$, $CaCl_2$, $MgSO_4$ and Phosphate buffer solution, separately. Each solution was aerated for 15 to 30 min and then 300 mL of this solution was taken in each bottle. From here, 1.5-10 mL of given sample was taken in two bottles and two bottles were kept without sample solution for blank reading. The two bottles (one sample + one blank) were transferred into 500 ml Erlenmeyer flask containing 2.0 mL $MnSO_4$ and alkaline iodide reagent. Precipitates were formed after shaking for a while and allowed to stand for 15 min for settling. Then, 200 mL volume was decanted in 300 ml Erlenmeyer flask and 2 mL of sulphuric acid was added. Then the solution was titrated for initial dissolved oxygen (IDO) against sodium thiosulfate ($Na_2S_20_3$) using starch solution as an indicator, until the dark yellow color was changed light yellow color. The IDO was calculated using the formula given as follows:

$$IDO = (Volume\ used\ of\ sodium\ thiosulphate\ X\ molarity\ of\ sodium\ thiosulphate\ X\ 8000)/300$$

Where 8000 is weight of oxygen in mg, 203 is 200X300/300-4, 300 is total volume of the solution, 200 is total volume of the solution minus decanted volume and 4 is MnSO4 and alkaline iodide reagent (2mL).

The other two bottles (one sample + one blank) were kept in the incubator at 20°C for 5 days. After 5 days the two bottles (one sample + one blank) were transferred into 500 mL Erlenmeyer flask, 2.0 mL of MnSO4 and alkaline iodide reagent were added. Precipitates were formed after shaking for a while; stand for 15 min for settling. Then, 200 ml volume was decanted in 300 mL. Erlenmeyer flask and 2 mL of sulphuric acid was added. Then the solution was titrated for final dissolved oxygen (DOF) against sodium thiosulfate ($Na_2S_2O_3$) using starch solution as an indicator, until the dark yellow color was changed light yellow color. DOF was calculated using the formula given for the determination of I . D . O

BOD (mg O_2/L) was determined as follows:

$$\mathrm{BOD} = \frac{\mathrm{BOI} - \mathrm{DOF}}{\mathrm{Dilution\ factor}}$$

Where Dilution factor is (10 x No. of sample)/ Total volume of sample

Reduction of BOD and COD after the treatment of pharmaceutical effluent

One litre effluent was taken in 2000 mL beaker and pH was determined (4.59). Then, 12.0 g calcium oxide was added and stirred to attain the pH of experimental solution between 7.0 to 8.0. The stirring was continued for 2.0 h. After that the pH was determined that was 7.62. Finally, 8.0 g ferrous sulfate was added to attain the pH of experimental solution between 6.5 to 7.0. The stirring was continued for 1.0 h. After stirring, pH was determined (6.80). The sample was allowed to stand for 12.0 h. After the settling, sludge was formed, and water decanted from the sludge.

RESULTS AND DISCUSSION

The effluent generated from the pharmaceutical plant was studied regarding different parameters like physical and chemical properties i.e.; general characteristics, pH, COD and BOD. The samples were taken from different products (amoxicillin trihydrate, ampicillin trihydrate, cloxacillin sodium and flucloxacillin derivatives) cephradine, cephalexin, cefadroxil, cefaclore and cefixime (cephalosporin derivatives) for the analysis purposes. After the analysis, results were found entirely out of range, which was very dangerous for the environment. Such results were not accepted by the National Environmental Quality Standards (NEQS). The results are shown in the Table-II. Actually the contents of organic chemicals present in the effluent raised the COD and BOD values and these contents caused the environment to be polluted. The requirement of oxygen for anaerobic bacteria increased to decompose the polluted components. Due to this environment may suffer by the deficiency of oxygen. That's why the COD and BOD values increased due to polluted water and environment, caused pollution. Treatment was only to overcome such a drastic condition. So according to the situation, a method was developed for the treatment of wastewater. The raw materials of the method should be cheap and easily available. Samples were collected from the both plants (cephalosporin +penicillin) and mixed well for treatment. The first ten experiments were not performed successfully; experiment 1-5 showed that the pH of the solution was basic (out of range) after the addition of ferrous sulfate in experiment 6-9 showed the pH of the solution was acidic (out of range). So the parameter was found out of control but the eleventh experiment was performed well as per required. Effluent was treated as per method with lime and ferrous sulfate and analyzed. Results were satisfactory as shown in the Table-II. There was lot of difference in the results before and after treatment.

BOD and COD was in millions, color was dark yellow and the pH was acidic (4.0-5.0) before treatment but after treatment the color was changed (light brown), pH was neutral and BOD and COD values were in thousands. Similarly total dissolved solids were too high but settled down after the treatment and the values were satisfactory. The other impurities in the effluent were found in minute quantities i.e. in parts per million (ppm). The experimental work and analysis (Table-II) showed that the treatment could not only reduce the side effects but also allowed to use the wastewater for beneficial purposes so it had positive impact on the environment. Most of the pharmaceuticals and chemicals industries do not treat the wastewater and drain it as such generated by the formulation or processing. They should not do so because polluted environment is same for all and effluents should be treated before they are drained. In this field "The studied plant" is ahead one-step. This organization has a water treatment plant for the enhancement in the water treatment field.

Table I: Summary of pharmaceutical effluent treatment

Experiment No.	Volume (ml)	pH	CaO (g)	Stir (h)	pH	FeSO4 (g)	Stir (h)	pH	Settling (h)
01	1000	4.49	12.0	2.0	7.89	8.0	1.0	6.62	12.0
02	1000	4,56	12,0	2.0	7.78	8.0	1.0	6.67	12.0
03	1000	4.6	12.0	2.0	7.68	8.0	1.0	6.87	12.0
04	1000	4.74	12.0	2.0	7.60	8.0	1.0	6.81	12.0
05	1000	4.56	12.0	2.0	7.42	8.0	1.0	6.81	12.0
06	1000	4.69	12.0	2.0	7.63	8.0	1:0	6.81	12.0
07	1000	4.55	12.0	2.0	7.80	8.0	1.0	6.88	12.0
08	1000	4.50	12.0	2.0	7.60	8.0	1.0	6.71	12.0
09	1000	4.45	12.0	2.0	7.65	8.0	1.0	6.84	12.0
10	1000	4.59	12.0	2.0	7.62	8.0	1.0	6.8	12.0

Table II: Results of pharmaceutical effluent treatment

Exp.	pH	Before treatment		After treatment		Types of treatment	Remarks
		COD (mg O_2/L)	BOD (mg O_2/L)	COD (mg O_2/L)	BOD (mg O_2/L)		
01	6.65	127104	79858	2542.3	1597.6	CaO + $FeSO_4$	Suitable for irrigation
02	6.85	126914	68594	2538.3	1370.98	CaO + $FeSO_4$	Suitable for irrigation
03	6.66	119421	67858	2388.4	1357.16	CaO + $FeSO_4$	Suitable for irrigation
04	6.84	119811	62517	2396.2	1250.4	CaO + $FeSO_4$	Suitable for irrigation
05	6.71	120142	71599	2402.8	1431.98	CaO + $FeSO_4$	Suitable for irrigation
06	6.91	118941	620368	2373.8	1207.36	CaO + $FeSO_4$	Suitable for irrigation
07	6.92	121120	59742	2422.4	1194.84	CaO + $FeSO_4$	Suitable for irrigation
08	6.84	118824	62141	2346.5	1242.84	CaO + $FeSO_4$	Suitable for irrigation
09	6.69	117246	55623	2344.9	112.46	CaO + $FeSO_4$	Suitable for irrigation
10	6.88	115562	50254	2311.2	1005.08	CaO + $FeSO_4$	Suitable for irrigation

Remarks: The treatment of pharmaceutical effluent was carried out with lime and ferrous sulfate and it was observed that almost 98.0% reduction of COD & BOD has been achieved after the treatment.

CONCLUSION

The treated water using the described method can be used for agriculture purposes. The method was easy, useful and economical; however, it could further be improved for better results.

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