Research Article

Pharmaceutical Waste Water Treatment Methods for Small-Scale Industries

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ABSTRACT

The concerns about the presence of active pharmaceutical ingredients, solvents and raw materials that could be present in pharmaceutical waste water have increased rapidly. The traditional wastewater treatment methods such as sedimentation, filtration, chlorination, neutralization, activated sludge method, and aerobic and anaerobic treatment are not sufficient for the complete removal of active pharmaceutical ingredients from the water. To increase the effectiveness complementary methods like Membrane Filtration, Total Dissolved Solid and Total Suspended Solid, Colony Forming Unit, Biological Oxygen Demand, and Ion Exchange Activated Carbon Methods are used in the small pharmaceutical industries. This study includes these complementary treatment methods along with traditional methods that can be used in small scale laboratories of small-scale industries in an easy and cheap way. The paper concludes that the tests can be performed in large as well as small scale industries to avoid the wastage of water and to reuse it.

Keywords: Pharmaceutical, Wastewater, Active Ingredient and Treatment.

INTRODUCTION

Pharmaceutical wastewater is generally characterized by high toxicity and the presence of refractory compounds that limit its biodegradability, making it a potential threat to the natural environment and wastewater treatment plants, if not handled properly. A broad spectrum of substances with significant variations in their structures, functions, behaviours, and activities are included by the word "pharmaceutical." They are used in people and animals to treat illness, prevent infection, and lessen symptoms. They were created to have a biological impact.[1]

Pharmaceutical wastewater can occasionally have a high chemical oxygen demand due to its mixture of organic and inorganic components, which include modest amounts of intermediates and products, catalysts, additives, reactants, and wasted solvents.[2]

COD levels in some pharmaceutical effluent might reach 40,000 mg/L.[3] Globally, around half of the pharmaceutical waste fluids generated are disposed of without any special handling.[4] Therefore, before being disposed of, pharmaceutical wastewater must be properly treated.[5]

MATERIALS AND METHODS

Materials:

Industrial wastewater, Aeration pump, Resin, HCl, Potassium dihydrogen phosphate, Disodium hydrogen phosphate, Ammonium chloride, Sodium oxide, Potassium iodide, Calcium carbonate, Magnesium sulphate, Ferric chloride, Thiosulphate solution.

Methods:

Physical methods:

In between all the physical methods, in the laboratory, we have performed four procedures. These are- A. Sedimentation, B. Aeration, C. Filtration and D. Degasification. The physical methods are described in the Table 1 with figures and legends.

The steps involved in the process of wastewater treatment through physical methods are as follows:

Table 1: Illustration describes physical methods with figures.

Different physical methods
A. Sedimentation
 Figure 1(a): Industrial waste poured into a beaker
 Figure 1(b): Settlement of solid particles from water
 Figure 1(c): Sedimentation of solid particles under the beaker

B. Aeration

Figure 1(d): Aeration of water by aeration pump

C. Filtration

Figure 1(e): Filter bed

Figure 1(f): Suction pump connected to the filter bed and collecting container

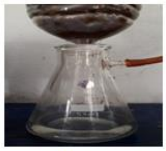


Figure 1(g): Collection of purified water

D. Degasification

Figure 1(h) and 1(i): Degasification of water by sonicator

A. Sedimentation:[6]

1. Pour the Industrial wastewater into a beaker represented in Figure 1(a).

2. Allowed it to stand for 7 days.

3. Solid particles settled down by the gravitational force represented in Figure 1(b).

4. Solid particles precipitated into the bottom of the beaker represented in Figure 1(c).

5. Pour the clear water into another beaker.

B. Aeration:[7]

1. Into the clear sedimented water an aeration pump is attached represented in Figure 1(d).

2. Allowed to aerate for 4 hours.

3. Then the pump is removed.

4. Aerated water in the beaker was taken out.

C. Filtration:[8]

1. Filter was prepared by the following way represented in Figure 1(e):

a. A container with wholes at the bottom was taken.

b. Into that some stone chips were put into the lower layer.

c. Sands were kept in the middle layer over it.

d. Into the top most layer there was crushed activated charcoal.

2. Then the container was attached to a suction pump for efficient filtration represented in Figure 1(f).

3. The water passed through the layers of the Sand Filter and filtrate was collected represented in Figure 1(g).

D. Degasification:[9]

1. An adequate amount of filtered water was taken in a beaker.

2. The beaker is taken to the 'sonicator'.

3. The sonication started and the time was set up to 2 hours represented in Figure 1(h) and Figure 1(i).

Table 2: Illustration describes chemical methods with figures:

Different chemical methods

A. Neutralization

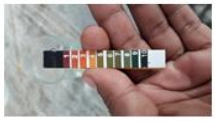


Figure 2(a): pH paper

Figure 2(b): Colour change in pH paper

Figure 2(c): pH was maintained at neutral by adding NaOH solution

B. Adsorption

Figure 2(d): Adequate amount of water was poured into the burettes

Figure 2(e): Into the bottom of the burette a beaker is placed to collect the adsorbed water

C. Ion exchange

Figure 2(f): Resin ionic beds in funnel

Figure 2(g): Preparation of cationic bed was prepared by 0.1 N HCl

Figure 2(h): water was passed through the ion charged resins

Chemical methods:

In between all the chemical methods the performed methods are (as described in Table 2):

A. Neutralization.

B. Adsorption.

C. Ion exchange.

The steps involved in the process of wastewater treatment through chemical methods are as follows:

A. Neutralization:[10]

1. 200 ml of water is taken in a beaker.

2. The pH of the water was checked represented in Figure 2(a).

3. The pH was acidic in nature represented in Figure 2(b).

4. The pH was maintained at neutral by adding a base, NaOH (0.1 N) represented in Figure 2(c).

B. Adsorption:[11]

1. Two burettes are taken.

2. The tip of the burette cotton was placed as a membrane.

3. Silica gel was introduced into the burette.

4. An adequate amount of water was poured into the burettes represented in Figure 2(d).

5. Burettes were allowed to stand for 5 hours.

6. Into the bottom of the burette a beaker is placed to collect the adsorbed water represented in Figure 2(e).

C. Ion exchange:[12]

1. Resin ionic beds (in the funnel) were prepared represented in Figure 2(f).

2. A cationic bed was prepared by HCl (0.1 N) passing through the resin into a funnel to make it cationic represented in Figure 2(g).

3. An anionic bed was prepared by adding NaOH (0.1N) through the resin.

4. The water was passed through the ion-charged resins (represented in Figure 2(h).

Table 3: Illustration describes the preparations involved in BOD estimation:

Procedures involved
1. Preparation of Phosphate buffer (pH 6.8)  Figure 3(a): Preparation of phosphate buffer
2. Preparation of azide reagent  Figure 3(b): Preparation of azide reagent
3. Preparation of the dilution water  Figure 3(c): Preparation of dilution water
4. Determination of Biological Oxygen Demand for sample water  Figure 3(d): BD Bottles  Figure 3(e): incubated BOD bottles (1 sample and 1 blank).
5. Test for dissolved oxygen  Figure 3(f): Manganous sulphate solution with sample  Figure 3(g): Precipitate form in bottom portion of the beaker  Figure 3(h): The precipitate was dissolved by mixing  Figure 3(i): Starch indicator solution  Figure 3(j): Blackish brown colour sample solution  Figure 3(k): Sample solution titrated with 0.025N sodium thiosulphate solution.  Figure 3(l): Blue colour was disappeared at the end point of titration

Biological Oxygen Demand (B.O.D):

Generally, it is assumed that the oxygen consumption rate is directly proportional to the concentration of organic matter present in the industrial wastewater.

For performing the B.O.D. we need to go through the following processes-

1. Preparation of phosphate buffer solution.

2. Preparation of the azide reagent.

3. Preparation of dilution water.

4. Determination of Biological Oxygen Demand of the sample water.

5. Test for dissolved oxygen.

6. Preparation of starch indicator

1. Preparation of Phosphate buffer (pH 6.8) represented in Figure 3(a)**:** For 10 ml

- 0.085 gm of Potassium di-hydrogen phosphate was taken.
- 0.334 gm of Disodium hydrogen phosphate was taken.
- 0.034 gm of Ammonium chloride was accurately weight and mix with water to prepare ammonium chloride solution.
- All the ingredients are dissolved in water and volume was adjusted up to 10 ml.

2. Preparation of azide reagent represented in Figure 3(b)**:** For 10 ml

- 5 gm of NaOH was accurately weighted.
- 1.35 gm of KI was also weighted.
- These two ingredients were mixed with distilled water.
- 0.1 gm of azide is dissolved into this water.
- Volume was adjusted up to 10 ml with distilled water.

3. Preparation of the dilution water represented in Figure 3(c): For 1200 ml

- 1200 ml of distilled water was taken in a beaker.
- It was aerated for almost 12 hours.
- It was kept for about 6 hours at 200C.
- Add 1.2 ml of 27.5% w/v solution of calcium carbonate.
- Add 1.2 ml of 22.5% w/v solution of magnesium sulphate.
- Add 1.2 ml of 0.15% w/v solution of ferric chloride.
- Add 1.2 ml of phosphate buffer solution.
- All the ingredients are mixed properly and allow standing for 2 hrs.

4. Determination of Biological Oxygen Demand for sample water:

- 300 ml of 4 BOD bottles were taken represented in Figure 3(d).
- 10 ml of samples was added to 2 BOD bottles and fill the remaining volume with dilution water.
- In remaining 2 BOD bottles are filled with only dilution water for blank.
- After filling the bottles are immediately closed so that any air bubbles should not be present in the bottles.
- Mark the bottles as blank and sample with the help of a marker.
- 1 sample and 1 blank bottle was incubated at 20°C for 5 days represented in Figure 3(e).
- The remaining 1 blank and 1 sample bottle were analyzed immediately for dissolved oxygen.
- The incubated 1 sample and 1 blank bottle was also analyzed for dissolved oxygen.

5. Test for dissolved oxygen:

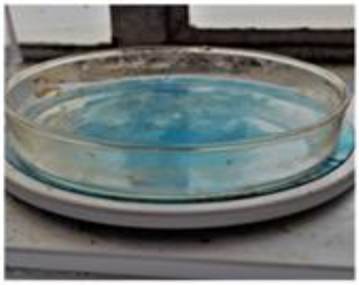
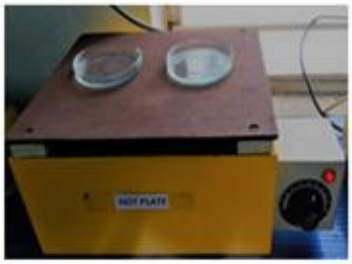
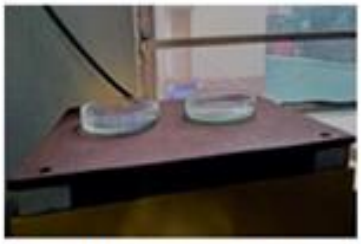
- 2 ml of 36.4% manganous sulphate solution was prepared and added to the sample by inserting the tip of the pipette so that the drops of the solution could allow the oxygen into the solution represented in Figure 3(f).
- 2ml of alkali-iodide-azide reagent was added.
- Allow the solution to react with oxygen present in the sample.
- The precipitation was formed and settled down at the bottom represented in Figure 3(g).
- 2 ml of conc. H_2SO_4 was added to the precipitation.
- The precipitate was dissolved by mixing represented in Figure 3(h).
- 203 ml of sample from individual 4 BOD bottles were taken and kept for titration.
- Preparation of sodium thiosulphate solution: 0.025 N sodium thiosulphate solution was prepared and taken into the burette.

Preparation of starch indicator:

- 1gm starch was taken and dissolved in 10 ml of boiling water. It is used as an indicator represented in Figure 3(i).
- The indicator was poured into each sample.
- The colour of the sample turned into a blackish brown colour represented in Figure 3(j).
- Each sample was titrated against 0.025 N sodium thiosulphate solution represented in Figure 3(k).

- Until the blue colour disappeared the titration was continued represented in Figure 3(l).
- The burette reading was noted down for each sample.
- The BOD value was calculated.

Table 4: Illustration depicts the procedures involved in TDS and TSS test

Procedures involved
Step-1 To measure the weight of the Petridish before putting in to the hot plate  Figure 4(a): Dry weight of Petridis was taken before putting those into the hot plate
Step-2 To keep two separate Petridish for TDS and TSS test  Figure 4(b): Petridish for TDS and TSS
Step-3 To place Petridish in warm condition in the hot plate for evaporation  Figure 4(c): Petridish were placed into the hot plate
Step-4 To check whether the sample contains any moisture or not  Figure 4(d): Water completely evaporated
Step-5 To place the Petridish at room temperature for complete drying procedure  Figure 4(e): Petridish, cool down at room temperature

Total Dissolved Solid (TDS) & Total Suspended Solid (TSS) Test (as described in Table 4):

- The dry weight of glass containers (Petridish) was taken before putting those into the hot plate represented in Figure 4(a).
- 10 ml of filtered water was poured into it for TDS and 10 ml of raw sample water was poured into the Petridish for TSS represented in Figure 4(b).
- Both the Petridish were placed into the hot plate represented in Figure 4(c).
- The Petridish were kept until the water completely evaporated (represented in Figure 4(d).
- After completion of evaporation, the Petridish were kept to cool down at room temperature represented in Figure 4(e).
- The present weight of the Petri dishes was measured.
- The amount of TDS and TSS were calculated.

RESULTS AND DISCUSSIONS

Physical procedure:

i. Sedimentation: Through this process of sedimentation solid particles present in the waste water got sedimented into the bottom of the beaker.

ii. Aeration: The process aeration produces bubbles in the water. Thus, air gets entrapped into the water.

iii. Filtration: The upper layer of the filter removed the organic compound and used as an absorbent. The middle layer removed the suspended particles present in water.

iv. Degasification: The process degasification removes all the gases dissolved in the wastewater.

Chemical procedure:

i. Neutralization: The sample was neutralized.

ii. Adsorption: Chlorine and some other metals were removed.

iii. Ion exchange: Dissolved ionic impurities were removed.

Biological Oxygen Demand (BOD):

Calculation:

Blank correction = (Burette reading for blank at initial stage – Burette reading for blank after 5 days incubation)

= (11.8 – 11.5) mg/L = 0.3 mg/L

Biological Oxygen Demand (BOD) = ((Burette reading for sample at initial stage – Burette reading of sample after 5 days incubation) – Blank correction) × Dilution factor

= (1.5 - 0.3) ×30 mg/L = 36 mg/L

The **BOD** of the present sample water is **36 mg/L.**

Total Dissolved Solid (TDS) & Total Suspended Solid (TSS):

Calculation:

Total Dissolved Solid (TDS):

Initial weight of the Petri dish = 43.23 (w_1)

Final weight of Petri dish = 53.40 (w_2)

Total Dissolved Solid (TDS) = (w_2-w_1) × 1000 × 1000 / 10 mg/L

= (10.17) ×1000×1000)/10 mg/L = 1017000 mg/L

Total Suspended Solid (TSS):

Initial weight of the Petri dish = 45.30 (w_3)

Final weight of the Petri dish = 53.29 (w_4)

Weight difference, W = (w_3 -w_4)

= 53.29-45.30 = 7.99

Total Suspended Solid (TSS) = (W × 1000 × 1000)/ 10

= 799000 mg/L

Therefore, the **TDS** of the sample water is 1017000**mg/L** and the **TSS** of the sample water is 799000 **mg/L.**

CONCLUSION

Through this project work, the wastewater is successfully treated which may be able to be recycled. In the experiments, all the simple and cheaper methods for wastewater treatment were used. These techniques can be easily performed in any standard laboratory. The wastewater was treated with physical, chemical and biological methods. Through these techniques, the contaminants i.e., heavy metals, inorganic compounds, and some ionic impurities can be removed and also the hard water is converted into soft water. So, it can be concluded that pharmaceutical wastewater can be treated in a simple and cheaper way. The treated water can be reused. It does not produce any harmful effects while discharging to the environment. It can be helpful and convenient for those pharmaceutical industries which do not have sufficient funds to treat the used contaminated water before discharging.

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