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Treatability Study of Pharmaceutical Wastewater by Coagulation Process

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Abstract : Attempts were made in this study to examine the effect of three coagulants on pharmaceutical waste water; the coagulation process for treatment of effluent of Pharmaceutical wastewater is effective. A doze of 30 mM/L FeCl₃, AlCl₃ and 60 mM/L FeSO₄gives COD reduction of 85%, 81% and 86.5% respectively at optimum pH of 4, 6 and 4 respectively. COD reduction was found to extremely depend on pH. The total COD reduction was depending on coagulation pH and functional groups present in effluent. In addition, optimal parameters of Coagulation process were determined to be 30 mM/L of FeCl₃ dosage, 30mM/L of AlCl₃ and 60 mM/L of FeSO₄. When treated effluent was controlled at pH 7.0, the pollutants could be further removed by sedimentation process. The overall Turbidity, COD, Chloride, Alkalinity, Acidity, Hardness and Total solids (TS) removal reached 90%, 91%, 88%, 47.1%, 78.7%, and 75.4% under selected conditions, respectively. Thus this study might offer an effective way for wastewater treatment of antibiotics manufacturer and pharmaceutical solids industry.

Keyword: Coagulants, COD, Pharmaceutical Wastewater, Treatment process's.

1.Introduction

The Present studies include the characterization of wastewater, containing impurities generated in the industry from different processing steps and units of effluent treatment plant. Performance appraisal of each unit of effluent treatment and possibility of augmentation. Final attention is given on treatability study of various parameters like COD, BOD HARDNESS etc. and compares the effect of coagulants with different pH. Due consideration is also given to the comparison of effluent characteristics parameters of effluent treatment plant with the State Pollution Control Board Effluent Quality standards discharged in different receiving bodies as per IS: 2490 (Part-I) 1974 and standards for liquid effluent for Pharmaceutical Industries. Toxicity tests are also done on treated effluent to study the effects of treated waste effluent on ecological environment before disposal [1].

Pharmaceutical industry consumes considerable volume of water for various manufacturing processes of drugs production. Water is also used and required for steam generation and other general purposes. The wastewater discharged is highly polluted in nature with highly variable characteristics such as temperature, colour, total solids, BOD, chemical oxygen demand, anions [2]. Due to highly polluting nature, it is not possible to discharge treated and untreated waste either into water course or on land without causing great damage. They

pose a great problem for environmental engineers.

Coagulation/precipitation (C/P) processes have been found to be cost effective, easy to operate, and energy saving treatment alternatives [3]. C/P processes have been mainly used for wastewater treatment to separate suspended and/or fatty particles [4]. The most widely used coagulants are alum; iron salts and lime [5]. The main function of coagulants is to flocculate colloidal particulates into larger particles that can be removed by sedimentation or flotation [6]. The mode of action is generally explained in terms of two distinct mechanisms: 1) neutralization of negatively charged colloids by cationic hydrolysis products and, 2) incorporation of impurities in an amorphous hydroxide precipitate, so-called sweep flocculation [6]. The relative importance of these mechanisms depends on factors such as pH and coagulant dosage. C/P has been used for the treatment of wastewater discharged from pharmaceutical industry.

The objective of the experiments is to investigate chemical coagulation followed by precipitation (C/P) using aluminum chloride, ferric chloride and ferrous sulfate for pretreatment of pharmaceutical Effluent (PE). The optimum pH values and coagulant dose were determined for each coagulant. Emphasis will be afforded to the removal efficiency of the COD, BOD5, TSS, Hardness, Alkalinity and Acidity. Moreover, characteristics of the floated and settled sludge were assessed. Initial investments as well as the operational cost of the treatment process were estimated.

2.Material and methods

2.1. Wastewater and analytical methods

The industrial wastewater used in this study was provided from Alpha Lab. Pvt Ltd. Company for manufacturing of pharmaceutical products (PCPs). The main surfactant used in this factory, is the anionic surfactant (sodium lauryl ether sulphate). Some other chemical compounds are also used in the formulation of different PCPs products, such as: Lignocane, Paracetamol, Amicasine, Cebixime Trihydrate, Quinodrum etc. Flow measurement of the wastewater indicated that the wastewater discharged is around 90 m3/d.

Physico-chemical analyses of 24 h composite samples were carried out according to APHA [7]. The analysis covered chemical oxygen demand (COD), biochemical oxygen demand (BOD5), total suspended solids (TSS), suspended solids (SS), total dissolved solid(TDS), Acidity ,Turbidity, Chloride Present, Hardness etc. All the parameter was determined according to APHA. In this study, we compare the effect of different coagulants like ferric chloride, aluminum chloride and ferrous sulphate on wastewater parameter.

2.2. Treatment processes

To develop design parameters for treatment of end of pipe effluent of the wastewater under investigation, coagulation-precipitation treatment schemes was studied. The coagulants used were ferric chloride, alum chloride, and ferrous sulfate. The optimum pH values and coagulant dose were determined for each coagulant. All coagulants were aided with lime. Lime has many positive effects. It adjusts the pH to the optimum value, acts as a coagulant aid, and improves sludge settle ability and stability. However, it may increase the dry solids content of the sludge by 20–30% [8].

Chemical coagulations were performed in jar test apparatus. 0.5 dm³ PWW sample was taken in 1 dm³ beaker. After this, the calculated amount of coagulants were aided and its pH was adjusted using 1 M HCL or 2 M NaOH. When the desired pH was maintained, it was kept for stirring in jar-test experimental set up. The PE sample with coagulants was rapid mixed (RM) at 70 rpm for 5 minutes followed by 20 min slow mixing (SM) at 40 rpm and 2 h quiescent settling. The supernatants were analyzed for COD. Effect of initial pH (pH₀) and mass loading of coagulants at optimum pH were performed. Other Parameters like BOD, DO, TS, TDS, TSS, Chloride, Acidity and Alkalinity was also studied.

3. Results and discussion

Table 1

3.1. Wastewater characteristics

Wastewater is produced from production lines, equipments, and floor cleaning operations. Main characteristics of wastewater are presented in Table 1. The BOD5/COD ratio averaged 0.46. A significant amount of COD (on average 40%) is in the form of insoluble material[9].

Average value
Yellowish
6
15
1920
500
16460
5460
11000
2030

3.2. Coagulation-precipitation (C/P) process

3.2.1. Effect of pH and Various Coagulants

The COD reduction of Effluent as the function of the initial pH for various coagulants is presented in Fig. (3.1). A doze of 60 mM FeCl₃, $AlCl_3$, $FeSO_4$ gives COD reduction of 68.4%, 80% and 91% respectively at optimum pH of 4,6 and 4. The coagulant dozes kept constant of 60mm. The iron based compound (FeCl₃, $FeSO_4$) have given maximum reduction in COD as compared to $AlCl_3$. With the $FeSO_4COD$ reduction was decreased from pH 4 to pH 8. With FeCl₃ coagulant the COD reduction increased from pH 2 to 4 and continuously decreased from pH 4 to 8. For $AlCl_3$ coagulant the COD reduction was found to increased from pH 2 to 8.

The carboxylic and phenolic groups present in Effluent coordinate with metal cations at low pH as compared to hydroxyl and aliphatic hydroxyl groups[10]. However coagulation /flocculation for a particular functional groups taking part in the coordination and complexation with metal cations depends on amount and types of functional groups[11].

The removal of dissolved organics during coagulation and precipitation with the metal salts at different pH value follows two distinct mechanisms at low pH; the effluent containing anionic organic molecules coordinate with metal cations and form insoluble complexes. At higher pH and elevated coagulant doses, the organics absorbed onto reforms flock of metal hydroxides and gets precipitated. The net result of two mechanisms is that the removal of dissolved organics compounds with different functional groups can occur over a wide range of pH and that maximum COD and color removed may occur at pH where the combine effect of both mechanisms is maximum[12].



Fig 3.1 Determination of optimum pH value at fixed dose of coagulants (60 mM/l).

3.2.2. Comparison of different coagulant for COD removal:

The effect of different coagulants, such as, ferrous sulphate, ferric chloride, Aluminum chloride, on the COD reduction of the wastewater at room temperature. For the assessment of the viability of the coagulation process, the cost comparison of different coagulants per unit of COD removed has been made. The costs of the coagulants have been taken from the open market. For the removal of the same amount of COD, the ferric chloride and ferrous sulphate are 12.3 and 18 times costlier than commercial alum or aluminum chloride[13].

The addition of different coagulant in the effluent and its flash mixing creates proper coagulant condition. Gentle mixing, thereafter-initiated flock formation, complexation and adsorption of the organics resulting in the precipitation and settling of the insoluble solids.

In order to determine the optimum dosage of the three coagulants for the removal of COD and other parameter from PE, different dosage of Fecl₃, FeSO₄ and AlCl₃ are used in experiments.

3.2.3. Effect of FeSO₄ coagulant dosage on COD removal

The effect of FeSO₄ dosage on COD reduction is presented in (Fig 3.2). It can be seen that the rate of COD reduction increase considerably till 60mM FeSO₄ loading. After this loading COD does not increase much. FeSO₄ coagulant dosage is optimum giving a COD reduction of 86.5% for optimum loading of 60 mM at optimum pH 4. The treatment of textile wastewater with ferrous sulfate, regulating pH in the range of 8.5–9.5 by lime, was proved very effective in removing COD (50–60%) from textile wastewater [14].



Fig3.2 Determination of optimum dose of ferrous sulfate at constant pH value of 4.

3.2.4. Effect of FeCl₃coagulant dosage on COD removal

The effect of FeCl3 dosage on COD reduction is presented in (Fig 3.3). It can be seen that the rate of COD reduction increase considerably till 30mM Fe3+ as FeCl3 loading. After this loading COD does not increase much.FeCl3 coagulant dosage is optimum giving a COD reduction of 85% for optimum loading of 30 mM at optimum pH 4. The optimum dose of a coagulant is defined as the value above which there is no significant difference in the increase of removal efficiency with a further addition of coagulant or flocculent [15].



Fig3.3 Determination of optimum dose of ferric chloride at constant pH value of 4.

3.2.5. Effect of AlCl₃coagulant dosage on COD removal

The effect of $AlCl_3$ dosage on COD reduction is presented in (Fig 3.4). It can be seen that the rate of COD reduction increase considerably till 30mM Al3+ as $AlCl_3$ loading. After the loading COD does not, increase much.AlCl_3 coagulant dosage is optimum giving a COD reduction of 81% for optimum loading of 30 mM at optimum pH 6.



Fig3.4 Determination of optimum dose of Aluminum chloride at constant pH value of 6.

4. Conclusions

- The coagulation process for treatment of effluent of Pharmaceutical wastewater is effective. A doze of 30 mM FeCl₃, AlCl₃ and 60 mM FeSO₄gives COD reduction of 85%,81% and 86.5% respectively at optimum pH of 4,6 and 4 respectively.COD reduction was found to extremely depend on pH. The total COD reduction was depending on coagulation pH and functional groups present in effluent.
- The pH of effluent was found to decrease with adding of coagulants. pH decreasing order was FeCl₃ > FeSO₄ > AlCl₃.
- The settling rate of flocculated sludge was found in order of $FeCl_3 > FeSO_4 > AlCl_3$.
- Based on all the experimental results we conclude that the ferrous sulphate coagulant gives the good results as compared to the ferric chloride and aluminium chloride coagulants.

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