

AMMONIACAL NITROGEN REMOVAL BY MAGNESIUM AMMONIUM PHOSPHATE (MAP) PROCESS FROM PHARMACEUTICAL WASTEWATER

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Abstract: In this study, the theoretical basis and affecting parameters of Magnesium Ammonium Phosphate (MAP) are studied and experimentally tested for Pharmaceutical Wastewater. The MAP process is applied to pharmaceutical wastewater for removal of Ammoniacal Nitrogen. The effect of pH, different mixing time, and different reagents for Mg source were tested in this study. The stoichiometric ratio of Mg^{2+} : NH_4^+ : PO_4^{2-} was controlled of 1:1:1 for effective removal of Nitrogen present in form of Ammonia. The removal of Chemical Oxygen Demand (COD) was also noticed during experiments. The effect of different reagents for Mg^{2+} like MgO , $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$ were compared during this study and $MgCl_2 \cdot 6H_2O$ is observed most efficient for removal of NH_4^+ -N.

IndexTerms- Ammoniacal Nitrogen, MAP, Pharmaceutical Wastewater, Stoichiometric ratio

I. INTRODUCTION

There are different form in which Nitrogen is present in the environment like ammonia (NH_3), ammonium (NH_4^+), and nitrogen gas (N_2), nitrite ion (NO_2^-), and nitrate ion (NO_3^-) [6][8]. The nitrogen present in form of Ammonia is called Ammoniacal Nitrogen. Nitrogen is not a common parameter present in wastewater [14]. Depending upon the pH of solution, the ammonia nitrogen present in water in form the ammonium ion (NH_4^+) or ammonia gas (NH_3) [8]. The removal of compounds containing Nitrogen is an important in wastewater treatment facilities due to its negative effect on sensitive inland and coastal waters. Eutrophication is result of presence of nitrogen in wastewaters. Due to the extreme standards for Ammoniacal Nitrogen, different methods for removal of Ammoniacal Nitrogen are developed. The different methods were studied from various literature for comparison purpose. There are vast numbers of reviews for Ammoniacal Nitrogen removal techniques and its theoretical summary is described below.

The immature method is irrigation and infiltration which are the cause for land pollution [10]. The Ammonia stripping is also used in industries but it requires higher capital and construction cost as well as maintained pH [10]. This method is not viable in cold conditions [6]. Ion Exchange is also sophisticated method which runs on terminology of exchanging Ammonium ions by ions of a different species in solution [6]. But it has complex regenerative system as well as ample pre-treatment of wastewater is required for maintaining lifecycle of resins. Another method is chemical oxidation of Ammonia by using Chlorine as an oxidizing material, it is also known as 'Breakpoint Chlorination' but it has disadvantages like building up of HCl as well as Total Dissolved Solids [10]. The mostly used treatment for Ammoniacal Nitrogen in industries is Biological Nitrification and denitrification, in which oxidation of ammonia to nitrate under aerobic conditions followed by reduction of nitrate to nitrogen gas [5]. In this method nitrifying and denitrifying bacteria are used, but the expensive aeration and large aeration tanks are trouble in this method [6].

The Magnesium Ammonium Phosphate (MAP) is the most potential physico-chemical treatment for removal of Ammoniacal Nitrogen from Pharmaceutical wastewaters [14]. This process has gained significance due to its efficiency of removing NH_4^+ -N. It precipitates crystals called Struvite, which is complex precipitation [17]. The basic reactions involved with this process are as below:



The outline of core theoretical features of Struvite precipitation is as below.

The precipitation generated from Magnesium Ammonium Phosphate (MAP) process is called 'Struvite', which has chemical formula of $MgNH_4PO_4 \cdot 6H_2O$ [17]. Struvite crystallizes as a white orthorhombic crystalline structure, which is composed of magnesium, ammonium and phosphate in equal molar concentration [5]. The parameters like pH, mixing time, and stoichiometric ratio of reagents depends on the crystal formation. The precipitation is done in two steps like nucleation and crystal growth [7]. The crystals are precipitated in pH range of 8-10[17] because of its alkaline nature [18]. Being an alkaline salt, it will completely dissolved in the acid solution so the alkaline conditions are favourable for forming the precipitations [18]. The mixing intensity and struvite precipitation are correlated because mixing gives turbulence and causes reduction in pressure which encourages struvite precipitation [15]. The molar ratio of reagents is also very important because sufficient amount of reagents are required for crystals to form.

Pharmaceutical industries have two arms: Active Pharma Ingredients (API) and Formulation Plant. These industries use both organic and inorganic raw materials, so characteristics of effluents are depending upon the raw materials consumed.

II. MATERIALS AND METHODS

The pharmaceutical wastewater used in this study was carried out from CETP, Ankleshwar. The basic characteristics of sample are shown in table 1:

Table 1 Characteristics of sample

Sr. No.	Parameter	Unit	Value
1	pH	-	12.80
2	NH_4^+-N	mg/L	2480
3	COD	mg/L	80000

MgO , $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$ were employed as magnesium ion sources and $Na_2HPO_4 \cdot 12H_2O$ was employed as phosphate ion source. pH was adjusted using 0.5 M Sulphuric Acid. All chemicals used in the experiments were of analytical grade. The amount of reagents was calculated by using constant molar ratio of $Mg^{2+}:NH_4^+:PO_4^{2-}$ to 1:1:1.

The experiments were conducted by taking 500 mL wastewater in 1000 mL beakers. The weighed chemicals were added in the beaker. The pH was measured by Digital pH meter and adjusted at 9 by using 0.5 M H_2SO_4 . Mixing was provided by magnetic stirrer. Mixing was provided for different time period of 30 minute, 60 minute, 90 minute and 120 minute. pH, Ammoniacal Nitrogen and COD were measured by standard methods prescribed as in APHA [1].

The experimental procedure is shown in Figure 1.

III. EXPERIMENTAL RESULTS

The results of experiments for precipitation at stoichiometric dose ($Mg^{2+}/NH_4^+/PO_4^{3-} : 1/1/1$) with pharmaceutical wastewater obtained are shown in graphs. There were different combinations taken for experimental purpose, which are: A1) $MgO + Na_2HPO_4$ A2) $MgCl_2 \cdot 6H_2O + Na_2HPO_4$ and A3) $MgSO_4 \cdot 7H_2O + Na_2HPO_4$. The mixing time of 30 minute, 60 minute, 90 minute and 120 minute was provided to all the combinations.

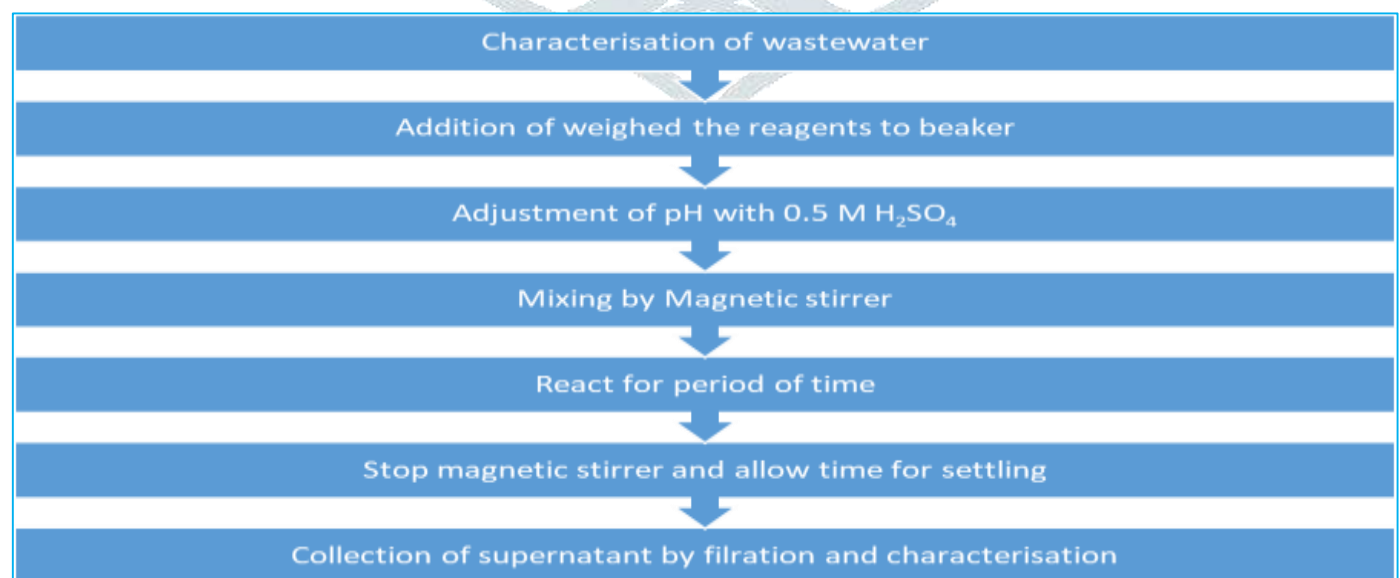


Figure 1 Methodology for Experiment

For the combination A1 (MgO + Na₂HPO₄) the mixing time provided was 30 minute, 60 minute, 90 minute and 120 minute, the pH was maintained at 9, due to alkaline nature of struvite. After mixing for appropriate time, the effluent was allowed to settle and supernatant was collected and measurement of COD and Ammoniacal Nitrogen was done. The Fig. 2 explains the reduction of Ammoniacal Nitrogen at different time interval and maximum reduction obtained was 706.5 mg/L for 90 minute of mixing.

Same procedure was given to combinations A2 and A3, as shown in Fig. 3 and Fig.4 maximum reduction was obtained at mixing time of 90 minutes. For combination A2, the maximum reduction observed was 454.83 mg/L.

The most effective mixing time was also 90 minute for combination A3, the maximum reduction was 499.4 mg/L for combination A3.

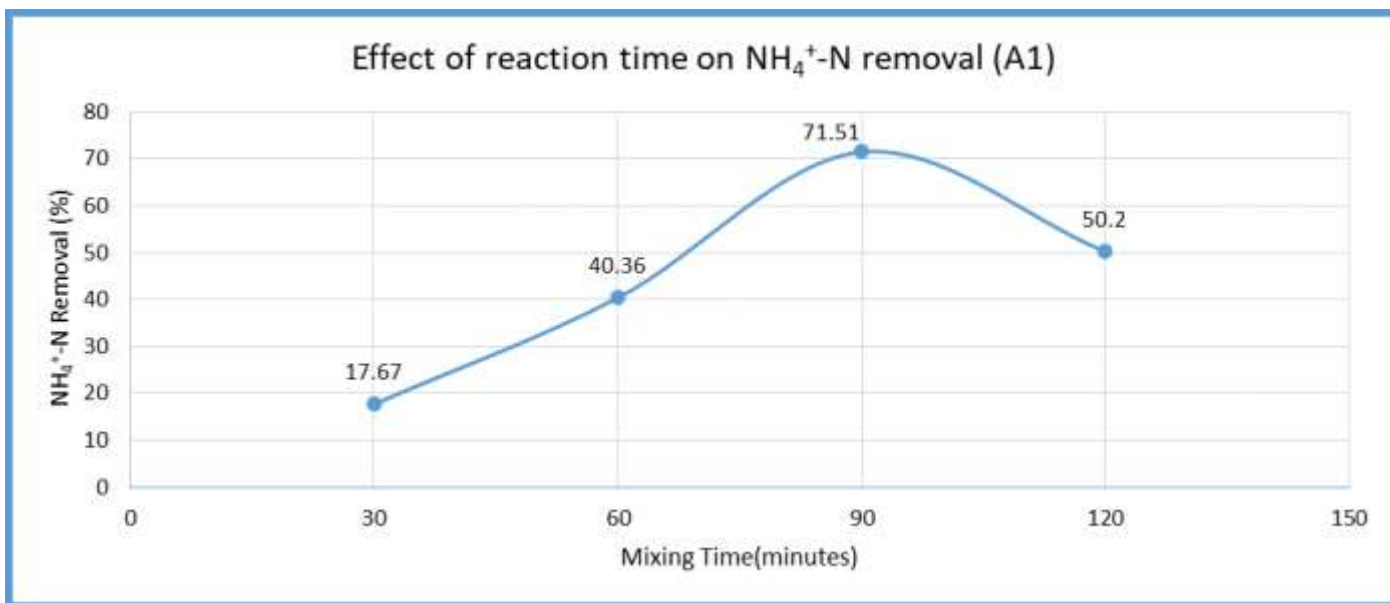


Figure 2 Effect of reaction time on NH₄⁺-N removal (A1)

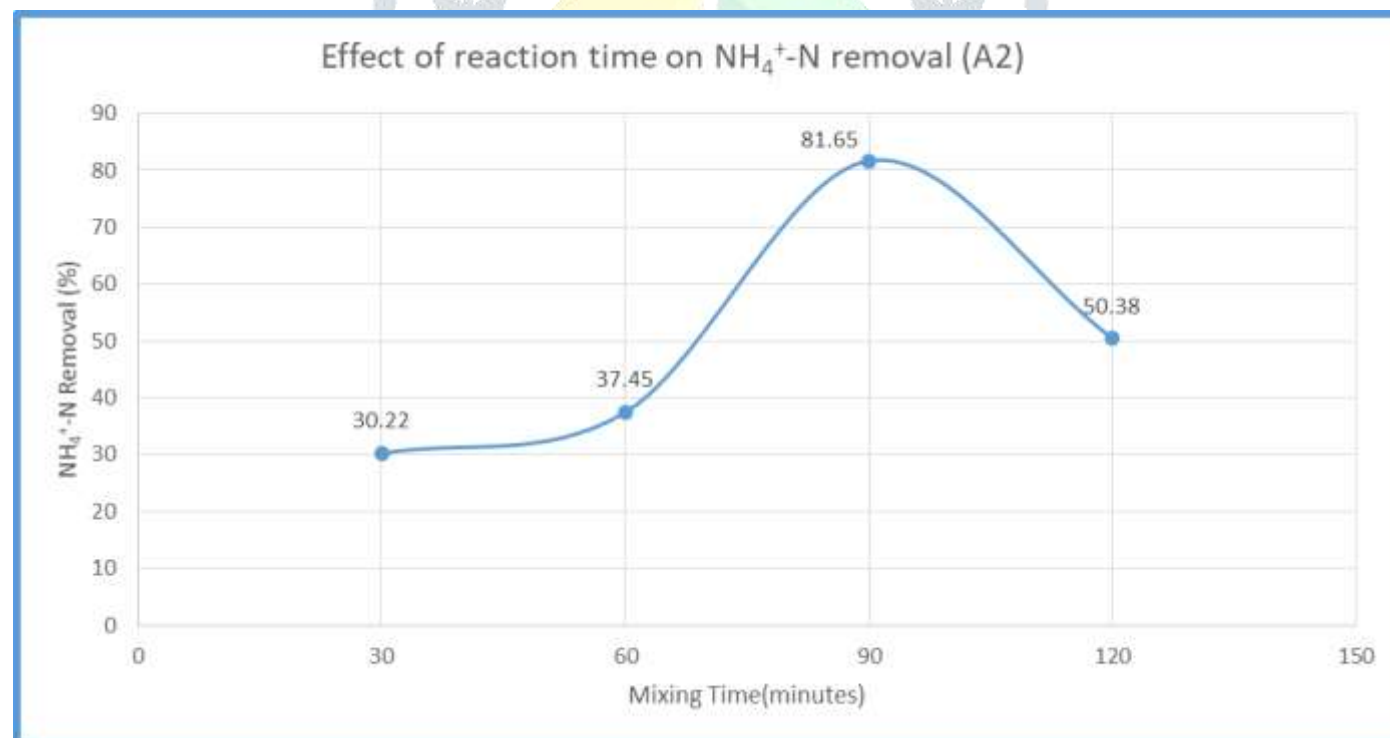


Figure 3 Effect of reaction time on NH₄⁺-N removal (A2)

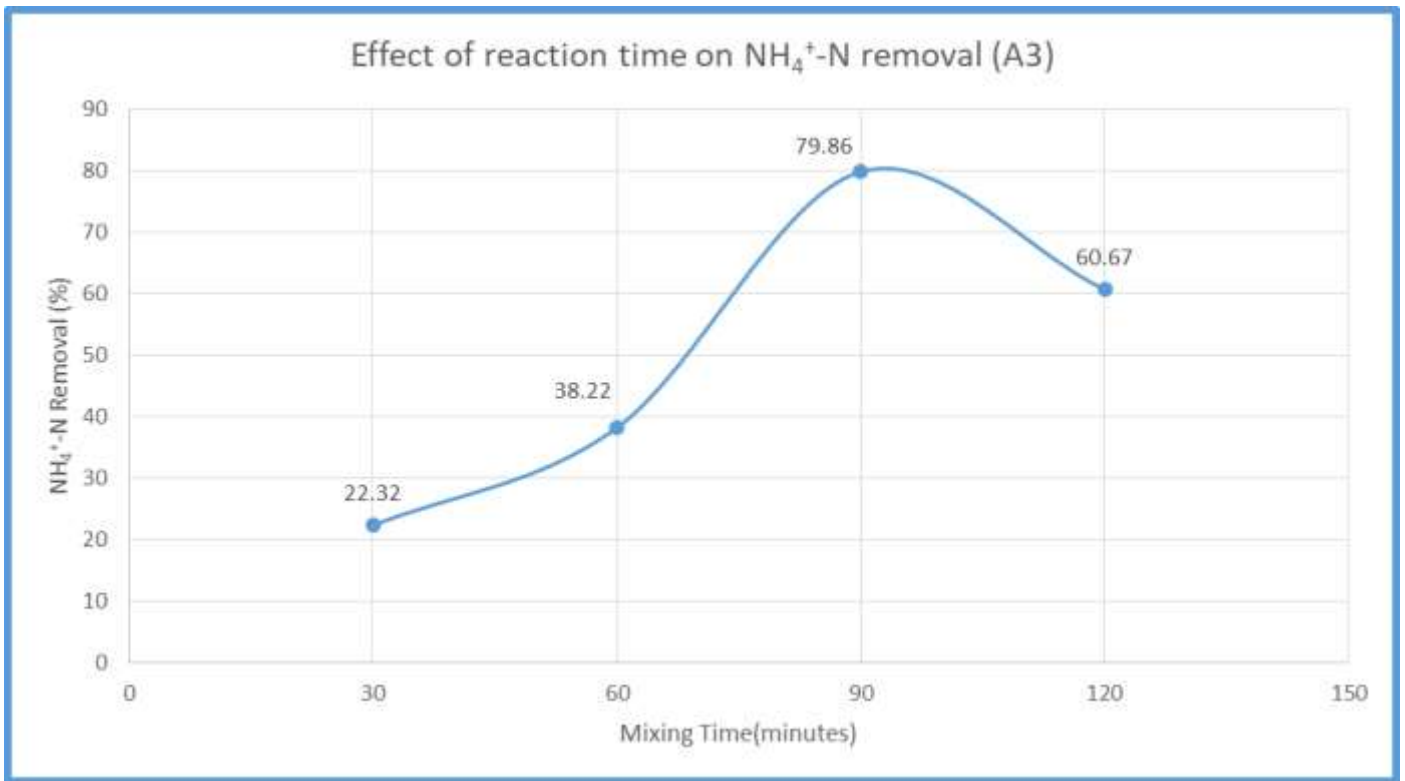


Figure 4 Effect of reaction time on NH₄⁺-N removal (A3)

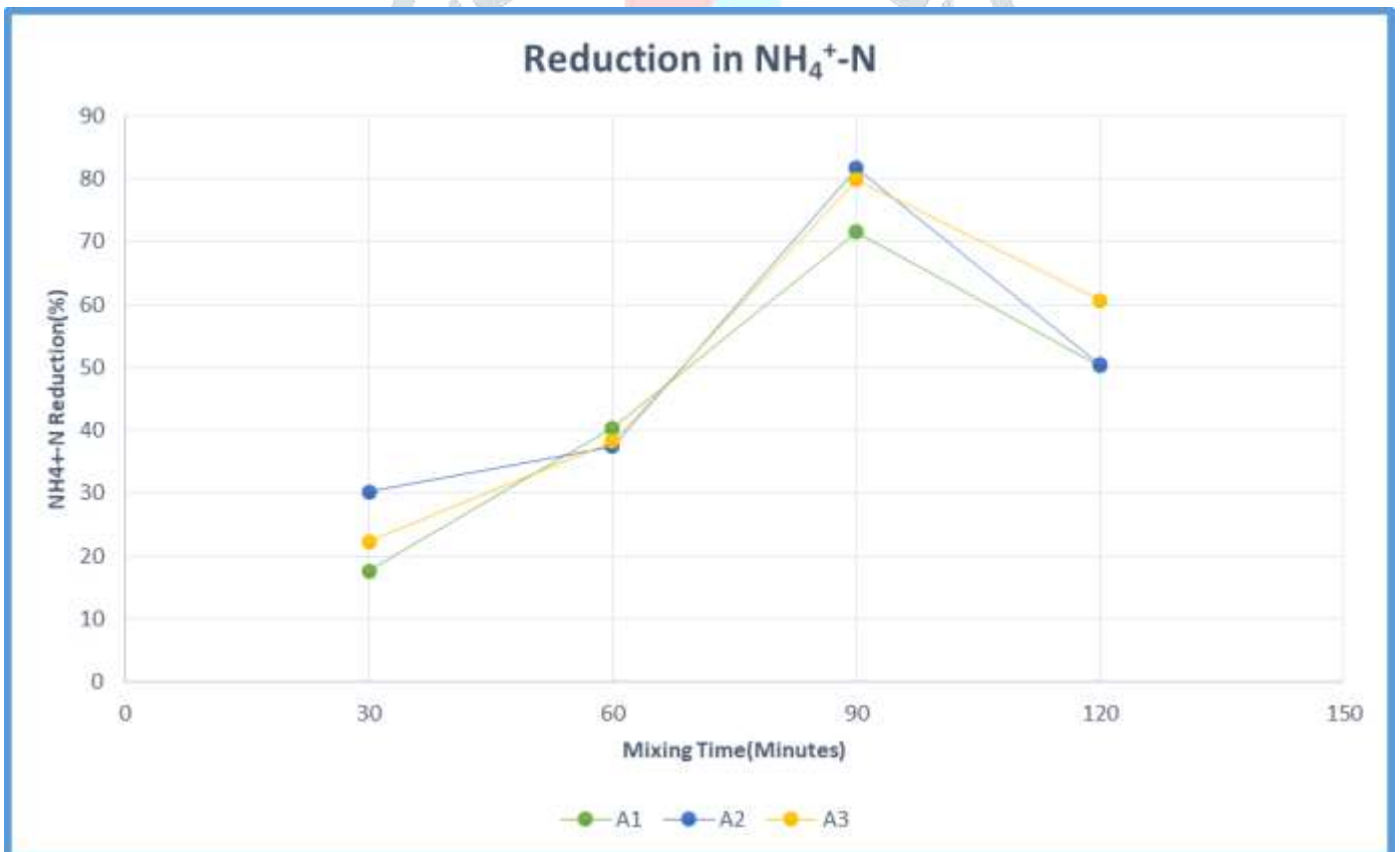


Figure 5 Comparison of reduction in NH₄⁺-N by combinations A1, A2 and A3

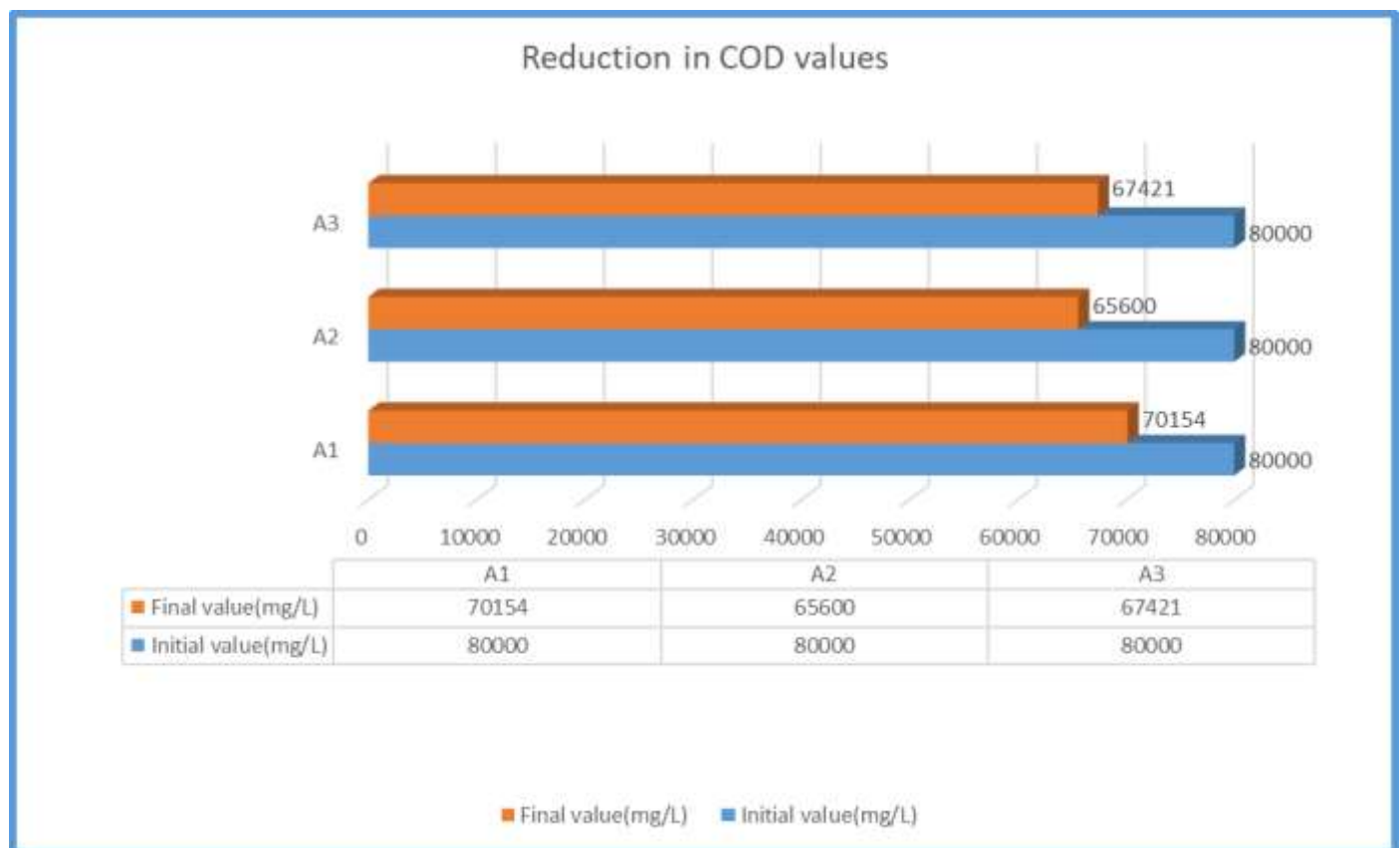


Figure 6 Reduction in COD values

IV. CONCLUSION

Physico-Chemical process called Magnesium Ammonium Phosphate (MAP) was applied for removal of $\text{NH}_4^+\text{-N}$ for pharmaceutical wastewater, the pH was maintained at 9 and the three combinations $\text{MgO} + \text{Na}_2\text{HPO}_4$ (A1), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4$ (A2) and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4$ (A3) with constant stoichiometric ratio $\text{Mg}^{2+} / \text{NH}_4^+ / \text{PO}_4^{3-} : 1/1/1$ were used to determine the removal efficiency of $\text{NH}_4^+\text{-N}$. Different mixing time of 30 minute, 60 minute, 90 minute and 120 minute were provided and based on experiment tests, conclusion is drawn that $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4$ was most efficient combination for removal of $\text{NH}_4^+\text{-N}$, compared to other combinations. Due to high solubility of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ compared to low solubility of MgO , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is more efficient, but due to low cost MgO can also be good option for this process. Mixing time is also an important parameter because the crystal formation was started at mixing time of 15 minute, maximum reduction of $\text{NH}_4^+\text{-N}$ was achieved at mixing time of 90 minute.

The MAP precipitation process is satisfactory with pharmaceutical wastewater, the COD will also reduce up to some level by using this treatment. Aside from addition of chemicals no other equipment is needed in this process, also the struvite can be used as fertilizers so this process can be suggested for green approach.

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