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Separation and recovery of mangenese- and cobalt catalysts from wastewater of PTA unit

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ABSTRACT

The goal of this work is separation and recovery of catalyst residue in wastewater and byproducts of PTA (poly terephetalic acid) unit. Catalyst recovery consists of separation the maximum amount of catalyst and changing the same into valuable compounds. The PTA unit uses mangenese- & cobalt catalyst for oxidation reactions. The byproducts, which contain catalyst, were burned. In the case of metal oxide recovery in the ashes of waste materials, we could solve the problem of the Petrochamical Company. This new method may help us to recover catalyst from wastewater in PTA unit, after which small amounts of ions may be absorbed in a column filled with special absorbent, in a way that the wastewater outgoing the column has no heavy metal ions. This method is both economical and may solve the environmental problems. In this method and under special pH conditions and time, it is possible to convert mangenese- & cobalt ions to metal-hydroxide precipitation, after which the same may be changed into mangenese- & cobalt-acetate. We may use it again as out going catalysts. As an important result of such work, is finding the exact conditions for recovery of this metal ion from wastewater.

KEYWORDS

Trephetalic acid;
Mangenese- & Cobalt acetate;
Catalyst;
Recovery;
Separation;
Environment;
Pollution.

INTRODUCTION

Some compounds such as mangenese- & cobalt-acetate are used as catalyst in order to synthesis of organic substances (as oxidizing agents). Such compounds are generally valuable and shall not be entered into the environment. The experts suggest different methods regarding separation and recovery from waste water, however prior to enter into the environment. One of the most important and proper separation methods is at the aqueous phase. In this method, they are obtained in salt form, in a way that subsequently their density in wastewater would be low. Such methods are practical due to economical reasons[1-3]. Pure terephetalic acid is used as a raw material for the production of polyesters. Terephetalic acid is also used as a favorable raw material for producing terephetalat resin. The latter is used for production of different packing materials, such as PET bottles[4-7].

After production and at the next phase, recovery and separation of the catalyst shall be performed. The obtained suspension is directed into the columns for due recovery, in a way that by increasing the heat and separating the solvent, a double-phased suspension is obtained. The same is then directed into a centrifuge (which makes the solid phase) for due separation. Now, the aqueous phase contains valuable catalysts in the form of precipitations, which shall be separated completely. The big problem of TA industry is preventing the catalyst waste. In order to do so an economical method which is also ecological, using which the mangenese- & cobalt catalyst is fully separated and recovered. In this method the heavy metals ions are not inserted into the environment. Hence, one of the biggest problems of the petrochemical industry may be solved, i.e. full prevention the heavy metals from entering into the environment.

EXPERIMENTAL

Equipment

1- Atomic Absorption Instrument, AA 220-Varian.
2- pH meter, ZPH 76 ATC.
3- Electerical furnance, Thermoline.

Chemicals

1- Cobalt (II) acetate, $Co(Ac)_2.4H_2O$ from Fluka Co. (pro analysis) Art # 60760.
2- Cobalt metallic powder from Merck Co. (pro analysis) Art # 12930.
3- Manganese (II) acetate, $Mn(Ac)_2.4H_2O$ from Merck Co. (pro analysis) Art # 60760.
4- Acetic acid 97% from Merck Co. (pro analysis) Art # 62.
5- Hydrochloric acid 37%, from Merck Co. (pro analysis) Art # 3172500.
6- Hydrazin hydroxide 24%, from Merck Co. (pro analysis) Art # 854298.
7- Buffer solutions 4, 7 & 9 from Merck Co.
8- Resin: Dowex 50W from Fluka Co. Art # 44463. (strong acid cation exchanger Sulfonic acid-matrix:gel-styrene DVB).
9- Twice distillated water.

Investigating the important factors regarding the amount of separated mangenese & cobalt

The goal of this investigation is finding the best conditions (pH, T & t) in order to separate mangenese- & cobalt ions from waste water.

pH effect

As the very first step, the temperature (T) and mixing time (t_m) have been kept as constant, while the pH values have been variable as followed: approx. 0.5 g cobalt acetate and 1 g manganese acetate were solved in 50 ml of double-distilled water. The concentration of Co and Mn was 2.370 gl^{-1} and 4.490 gl^{-1}, then a NaOH (0.1 M) solution is added to it, and hence the pH rises accordingly. The point of equivalent is shown in Figure 1. The equivalent point shows pH=10.5 as the favorable value for separation of cobalt and manganese. The aforementioned results were tested for due checking, after which the precipitation was washed and dried in 3 hours and at 80°C. In Figure 2 and 3 the optimal pH attitude is shown, i.e., 10.5 for of cobalt and manganese. After filtering, the obtained solution contains very small quantities of cobalt in ppm range. This was determined exactly by atomic absorption. These results are represented in TABLE 1 and 2. The above-mentioned experiment was repeated with a sample of wastewater, from the Petrochemical Company, and the gave the similar results.

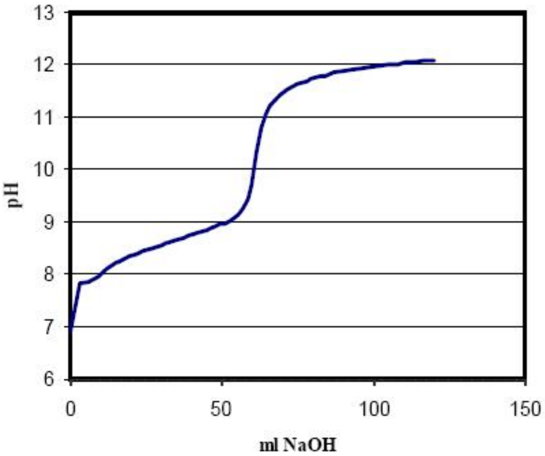

Figure 1: Titration curve of 0.040 M cobalt acetate and 0.082 M mangenese acetate solution with 0.1 M NaOH.

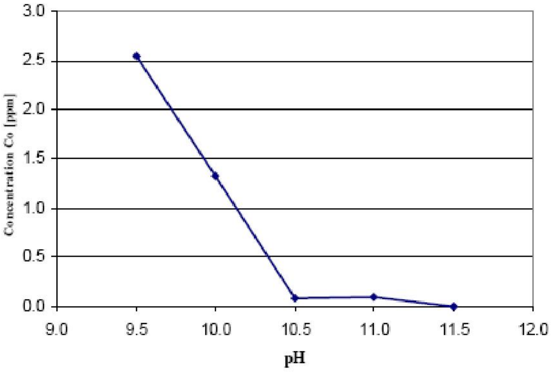

Figure 2: Influence of pH on amount of Co inons remained in wastewater after separation of precipitate (cobalt- & manganese hydroxide)

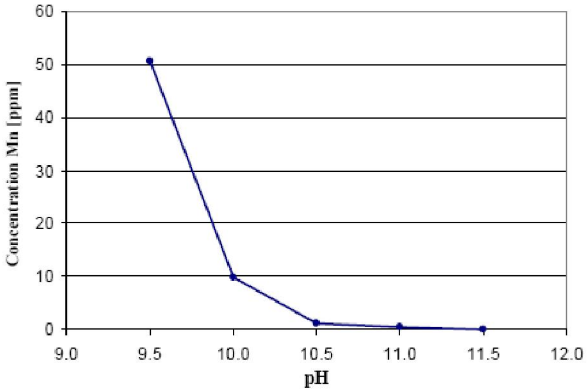

Figure 3: Influence of pH on amount of Mn inons remained in wastewater after separation of precipitate (cobalt- & manganese hydroxide)

TABLE 1 : Influence of pH on amount of Co ions remained in wastewater after separation of precipitate (cobalt- & manganese hydroxide)

pH	Experiment Serie 1	Experiment Serie 2	Experiment Serie 3	Average of Co concentration in Solution [ppm]
9.5	2.00	2.70	2.97	2.55
10.0	1.08	1.40	1.71	1.33
10.5	0.12	0.17	0.18	0.16
11.0	0.01	0.15	0.12	0.09
11.5	0.00	0.00	0.00	0.00

TABLE 2 : Influence of pH on amount of Mn ions remained in wastewater after separation of precipitate (cobalt- & manganese hydroxide)

pH	Experiment Serie 1	Experiment Serie 2	Experiment Serie 3	Average of Mn concentration in Solution [ppm]
9.5	52.20	61.40	37.40	50.66
10.0	11.20	9.40	8.50	9.70
10.5	1.40	1.40	0.50	1.10
11.0	0.20	0.80	0.14	0.38
11.5	0.00	0.03	0.00	0.01

Temperature effect

In this part a series of experiments were accomplished, in which pH and mixing time were kept constant. However, the temperature of the reactions were varied. As above, 0.5 g of cobalt acetate and 1 g manganese acetate were solved in 50 ml of double-distilled water, to which has been added 0.1 M of NaOH solution, and the metal hydroxide resulted. The temperature range was 0-60°C. at each temperature the experiment was accomplished and pertinent precipitation was filtered off, dried and weighed with due care (Figure 4 & 5).

Effect of mixing time (t_m)

The above-mentioned experiment was repeated again, however the mixing time of solution to complete the formation of metal hydroxide have been variable. The range of time was chosen as 1 to 60 minutes, after which the solution was filtered. The precipitation was washed and dried and duly weighed. The results of such experiments are shown in Figure 6 & 7.

Using the atomic absorption, the concentration of remained metal ions in the solution, after filtration of metal hydroxide precipitation was determine. The average value of several respective attempts was calculated as presented in TABLE 1 & 2.

In case if such values are compared with the initial concentration of metal ions, we may see that the entire amount of metal ions has been separated as metal hydroxide. However, such small amounts of metal ions are still harmful for the environment (TABLE 1 & 2). There were made a complete series of investigations. Finally, the product of Dowex50w was selected as the absorbance. Then the last solution, which still contained about one ppm metal ions, was flowered through a column (filled with Dowex50w). The column was 30cm long and 3cm wide. The flowered had then no metal ions, i.e. zero ppm. The concentration of metal ions in the last solution was measured using the atomic Absorption method. The measurements showed no metal ion in the final solution. This shows the high absorption capacity of the Dowex50w regarding Mn and Co ions.

Recovery of Cobalt

In this part of the work, the separated cobalt hydroxide precipitate was converted into cobalt acetate solution. This may be used again as a catalyst at the beginning of the process. In order to determine the solubility the following were made: 0.5g of dried cobalt precipitate was fully solved in 50ml HCl at 60°C. it was a clear pinkish solution. Then the same was repeated with acetic acid at reflax temperature and the same results obtained. Using the same method, a cobalt acetate solution was obtained which may be used in PTA process.

Extraction of cobalt from waste ash

In some petrochemical companies the waste materials are sent to be burned and converted into ash. We have used such ash and solved the same in HCl at a temperature of 60°C. After that the solution was filtered and, like above, was added to NaOH and converted into cobalt hydroxide.

Preparation of manganese and cobalt bearing ash

Some 10 g of manganese acetate and 3.5 g of cobalt acetate were weighted into a porcelain crucible and the same was placed inside a 900°C furnace for an hour and under normal temperature thereafter. After cooling down, the remaining ashes were weighted, which indicated the reduction of the weight thereof to an amount of 4.16 g. The aforementioned resulted ash was a black-reddish powder. The solubility of the ash was investigated in HCl, as the same for the previous part.

0.5 g of the aforementioned ash was weighted into 100 ml of 2 M HCl, and the mixture was stirred for an hour using a magnetic stirrer. Then the solution was filtered, after which the weight of the precipitation remained on the filter was determined as 0.3 g. In the next heating experiment for completion of the solubility of the precipitation were used an reducing agent. In the aforementioned experiment some 0.5 g of ash was solved in 100 ml of 2 M HCl. Then the temperature was fixed on 70°C, and some 0.2 ml of 4 molar hydrazine hydroxide was added thereto. The precipitation was completely solved and a transparent pinkish solution was resulted.

RESULTS & DISCUSSION

In Figures 1 and 2 the optimal pH attitude has been shown, which is 10.5 for separation of metal ions. After filtering, the obtained solution contains very small quantities of metal ions in ppm range. This was determined exactly by atomic absorption method. Such results have been represented in TABLE 1 & 2. This is of great importance, as using this method the concentration of metal in wastewater becomes quite small. As it may bee seen, the larger the pH value, the smaller becomes the concentration of metal ions in the respective solution. However, due to economical as well as technical reasons, a pH=10.5 was selected as optimal value. As we may see in TABLE 1 and 2 at the respective last column, the difference between the averages of remained manganese and cobalt concentration in pH= 10.5 and 11.5 is small. However, for the industry it is important that the minimal amount of chemicals is implemented for any process. The industry saves large quantities of chemicals. It shall be ensured that large amounts of NaOH are required to change the pH from 10.5 to 11.5. It is better to apply the separation of metal ions in two phases, rather than one. In the first phase, the precipitation occurs, while in the second the absorption is the case. For this reason, the ideal pH=10.5 was chosen. In the second part of experiments, the temperature range was chosen as 0-60°C. At each temperature the experiment was accomplished and the pertinent precipitation was filtered. Such results are shown in Figure 4 & 5. The results show that the optimal temperature was 20°C.

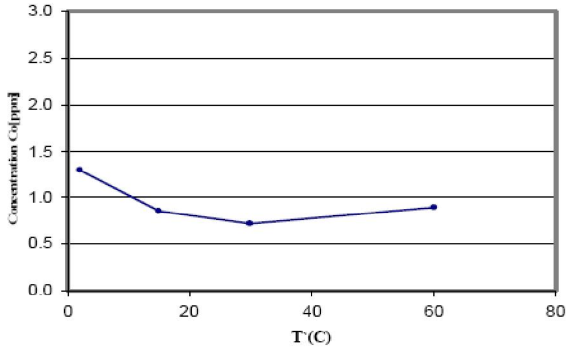

Figure 4: Influence of temperature on amount of Co inons remained in wastewater after separation of Co-hydroxide, pH=10.5.

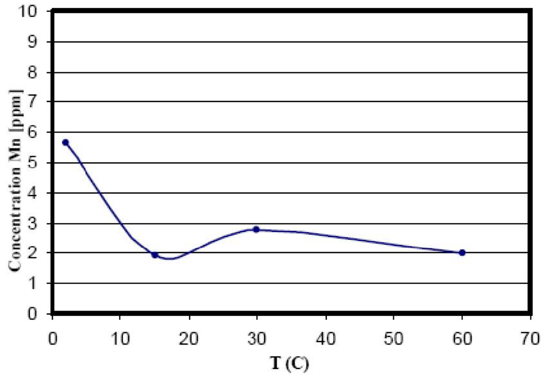

Figure 5: Influence of temperature on amount of Mn inons remained in wastewater after separation of Mn-hydroxide, pH=10.5.

In the third part of experiments, the mixing time has been investigated. As it can be seen in Figure 6 & 7, the optimal mixing time will be 30 minutes. Three factors were suited, namely pH, temperature and mixing time, in order to determine optimum conditions. According to this study, the pH value of 10.5 is ideal for conversion of Mn and Co ions to metal hydroxide. This is done by adding NaOH solution. The investigations also showed that the optimal temperature, which leads to maximal precipitation forming, is equal to 20°C. The next factor forming maximum amount of metal hydroxide was the mixing time. From TABLE 1 & 2 and Figures 6 & 7, it is evident that the favorable mixing time is 30 minutes. In order to summarize the results, as said before, the optimum conditions are as pH=10.5, T=20°C, t_m= 30 minutes. The precipitate was filtered and the concentration of metal ions in the solution was measured using an atomic absorption equipment.The method was quite successful, and the metal concentration in the solution can be made very small. Also, it was shown that the resulting solution was passed through a column. This column was filled with Dowex50w, as absorbance. This made it possible to decrease the amount of metal ions in wastewater, in a way that it reaches zero. The atomic absorption method has confirmed the above-mentioned results, which is an important point to be considered. The carried out experiments using ashes of waste materials from incinerator package showed that the same results have been obtained. It is evident that, conversion Mn & Co in ashes of waste materials to valuable metal hydroxide and then metal acetate is possible, which we may use the same as initial catalysts in PTA unit. It has also been shown that a simple solubility process can convert metal hydroxide into a metal acetate solution. This can be returned to PTA unit and used as a catalysts. To increase the solubility process, it is possible to add a small amount of hydrazine hydroxide (1-5% wt) and heat the same as reflax temperature. This leads to a clear solution.

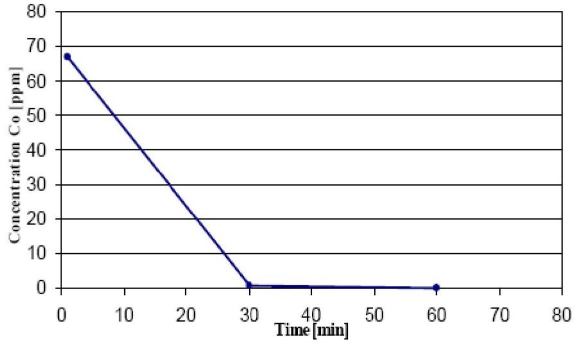

Figure 6: Influence of mixing time on amount of Co inons remained in wastewater after separation of Co-hydroxide, pH=10.5.

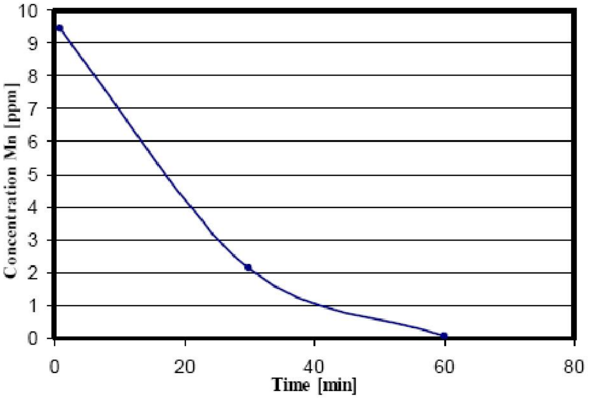

Figure 7: Influence of mixing time on amount of Mn inons remained in wastewater after separation of Mn-hydroxide, pH=10.5.

As described earlier, one of the biggest problems in the petrochemical industry has been solved in this work. With the proposed method a large loss of catalysts in the PTA industry was prevented from occurring. On the other hand, a big problem, namely environmental pollution by manganese and cobalt, was also solved. Using this method leads the Mn & Co concentration in waste water to be duly disappeared. This all results are summarized in Figure 8.

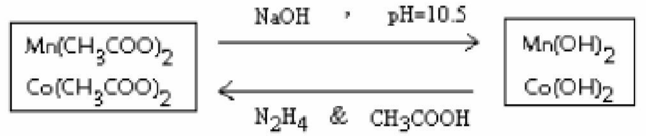

Figure 8: Sumarized illustration of methods for recovery of manganese- and cobalt catalysts from PTA unit.

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