STUDIES OF OXIDATION ORGANIC PHOSPHORUS BY MEANS OF FERROUS SULFATE AND FENTON'S REAGENT

Lucyna Przywara

University of Bielsko – Biala
ul. Willowa 2, 43 – 309 Bielsko – Biala
Fax. +48338125780, e-mail l.przywara@ath.bielsko.pl

Abstract

Removal of phosphorous is required as a measure preventing surface water eutrophication. Phosphorous can be removed by chemical precipitation with iron or alum reagents, or biologically. Lime used for phosphorous removal from food production industrial waste water leads only to removal of phosphates leaving organic phosphorous present in phospholipides in the wastewaters.

Investigations were carried out to remove the organic phosphorous by precipitation with ferrous sulfates and chemical oxidation using Fenton's reagent. Ferrous sulfates was used in the form of commercially available product PIX. The industrial effluents preliminarily treated with lime have constituted the substrate in our investigation. The waste water had an initial content total phosphour in the range of 4.3 to 41.7 mg P/l. Varying doses of PIX and Fenton's reagent were used, and the effects have been evaluated by measuring the concentration of total phosphorous. Moreover, the effects of aforementioned reagents addition on COD removal from wastewater were investigated. Depending on the dose of PIX used and pH decrease, the remained total phosphorous varied. The carried out research with PIX has shown a possibility of total phosphours removal in the range of 24 % to 80% at pH 5.5 – 8. At pH of about 3 almost a complete removal of total phosphorous was achieved.

Introduction

Phosphorus is an essential element for all living organisms and its utilization has promoted the development of agriculture and industry. The modern society does not use phosphorus resources in a sustainable way: phosphates are manufactured from phosphate – containing rock, then are consumed in agriculture and industry, finally go into soil, rivers and the sea. This, on one hand, is exhausting the limited phosphate deposits which are unevenly distributed in the world, on the other hand, has caused eutrophication of water bodies (1).

In waste water phosphorus is found in the pentavalent state tetrahedrally coordinated to oxygen atoms or hydroxyl group. The phosphate group occurs as ortho – phosphoric acid, as condensed phosphates, in which two or more phosphorus atoms are joined by P – O – P bonds, or as organic phosphates in which P – O – C linkages are present (2).

Phosphorous can be removed by chemical precipitation with iron or alum reagents, or lime. Chemical treatment methods (usually chemical precipitation) enabled the removal phosphorus in a high degree. But lime used for phosphorous removal from food production industrial waste waters, leads only to removal of phosphates leaving organic phosphorous present as phospholipides in the wastewaters. The aim of the present study was the removal the organic phosphorous by precipitation with ferrous sulfates and chemical oxidation using Fenton's reagent.

The Fenton's reagent it is a mixture of hydrogen peroxide and ferrous salt. In many cases Fenton 's reagent can oxidize organic compounds to carbon dioxide and water or to low

molecular carboxylic acids which are less toxic than their precursors (3). The Fenton reagent is used as a source of hydroxyl radicals. The hydroxyl radicals are a very powerful and effective non-selective oxidizing agent. The main advantage of Fenton 's reagent over other $OH^{\bullet}$ radicals generating systems is its simplicity: the chemicals are commonly available and there is no need for special equipment like UV lamps (4). The oxidation mechanism of organic compounds by Fenton reagent is very complex and occurs in the following stages:

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\bullet} + Fe^{3+} + OH^{-} \quad (1)$$
$$A + OH^{\bullet} \rightarrow A_{OX} \quad (2)$$

where: A – organic compound
A_{OX} – oxidation products.
Reaction (1) shows the generation of hydroxyl radicals, which react with the organic compounds in reaction (2).
Probably the PIX and Fenton reagent may be used to oxidation of organic phosphorus and precipitation.

Methodology

The study was carried out in laboratory scale. Two series (series 1, series 2) of investigation have been carried out with ferrous sulfates at pH values ranging from 5.5 to 8, and three (series 3, series 4 and series 5) for Fenton's reagent and ferrous sulfates at pH values about 3.
Ferrous sulfate was used in the form of commercially available product PIX. The industrial effluents preliminarily treated with lime have constituted the substrate in our investigations.
The precipitation experiment were carried out in a batch system
Chemicals were added and mixed for 3 min under rapid mixing condition (100 rpm) and the solution was mixed at slow flocculation for 15 min after rapid mixing. After allowed settling for 30 min, pH, temperature, redox potential, total phosphorus, and the chemical oxygen demand of the supernatant were measured.
All chemical determinations were done in accordance to the Standard Methods for the Examination of Water and Wastewater, 19 th Editon (5).

Results

During the first and second series the total phosphorus concentration was rather high in average 30 mg P/l for series 1 and 36 mg P/l for series 2, simultaneously phosphates very present on a level of 0.8 mg P/l. The investigations with PIX carried out at three different values of pH namely: 5.5, 6.5 and 8. All of the results of series 1 are presented in table 1, those of series 2 in table 2.

Tab.1. The results of series 1

Examinations	Unit	Waste water	SERIES 1		
			PIX - pH= 5.5 dose - 1.25ml/l	PIX - pH= 6.5 dose – 0.9ml/l	PIX- pH= 8.0 dose – 0.8 ml/l
pH		10.94	5.55	6.49	7.90
Temperature	°C	34.1	30.4	30.5	32
Conductivity	μS/cm	8470	8380	8280	8190
ORP	mV	-373	+1.9	- 141	- 325
Phosphates	mg PO_4/l	2.24	1.1	0.48	0.32
Total phosphorus	mg P/l	29.8	6.4	14.2	21.5

The total phosphorus removal efficiency depended on the value pH, which depended on the added dose of PIX. It is found that the lower the pH was, the lower the lower was the concentrations of total phosphorus in the treated waste waters. Practically the removal

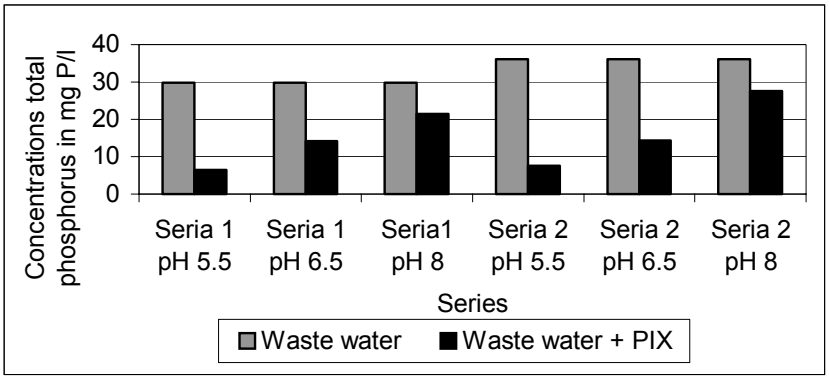
efficiencies of total phosphorus were in both series at the same level, depending on the value of pH.

Tab.2. The results of series 2

Examinations	Unit	Waste water	SERIES 2		
			PIX - pH = 5.5 dose - 1.7 ml/l	PIX - pH = 6.5 dose - 1.45 ml/l	PIX - pH = 8 dose – 1.1 ml/l
pH		11.40	5.47	6.45	8.00
Temperature	°C	40.1	35.4	36.3	35.4
Conductivity	μS/cm	10 180	9490	9370	9280
ORP	mV	- 334	+ 166	+ 55	+ 40
Phosphates	mg PO_4/l	1.4	0.12	0.45	4.19
Total phosphorus	mg P/l	36.19	7.6	14.3	27.6
COD	mg O_2/l	1425	902	1035	1343

In average an 80 % removal of total phosphorus was obtained at pH = 5.5, 55% at pH=6.5 and only 26 % at pH=8. As shown the total phosphorus removal efficiency decreased with the increased value of pH. For both series the maximum total phosphorus removal efficiencies were achieved for pH = 5.5, and minimum for pH =8. Figure 1 shows the effect of total phosphorus removal dependent on value pH

Fig.1 The effect of total phosphorus removal dependent on the value of pH



The purpose of further experiments was the evaluation of the removal efficiency of total phosphorus using PIX and/or Fenton's reagent at low pH. The research (series 3,4,5) were carried out using wastewaters having different levels of total phosphorus and COD.

The waste water had an initial total phosphorus in the range of 4.25 mg P/l to 16.2 mg/l, and COD in the range of 953 mgO_2/l to 1664 mg O_2/l.

During the investigation with PIX, an almost total removal of total phosphorus was obtained. The concentration of total phosphorus was on a level of 1 milligram per liter in treatment waste water. For the Fenton's reagent, removal to a level of several milligrams per liter was achieved. The results depended on the used dose of chemicals. The dose of PIX and Fenton's reagent depended on initial value pH. If the pH of treated waste waters was high, than the dose of chemicals had to been increased.

All the results of series 3, 4 and were presented in table 3, 4 and 5, respectively. Figure 2 shows the concentrations total phosphorus in wastewater after reagents addition.

Tab.3. The results of series 3

Examinations	Unit	Waste water	Series 3	
			PIX – pH = 3 dose – 3 ml/l	Fenton's reagent 10 ml/l $FeSO_4$ – 20 % 2 ml/l H_2O_2 – 30 %
pH		11.15	3.05	4.86
Temperature	°C	18.8	19.4	19.1
Total phosphorus	mg P/l	8.4	1.17	2.8
COD	mg O_2/l	953	592	559

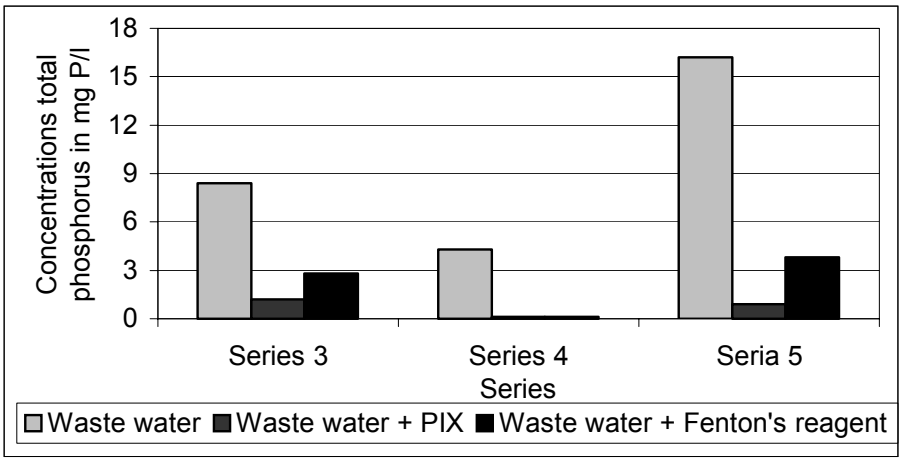
Tab.4. The results of series 4

Examinations	Unit	Waste water	Series 4	
			PIX - pH= 3 dose – 6 ml/l	Fenton's reagent 15 ml/l $FeSO_4$ – 20 % 6 ml/l H_2O_2 – 30 %
pH		11.54	2.90	3.08
Temperature	°C	18.8	19.1	19.3
Total phosphorus	mg P/l	4.25	0.04	0.06
COD	mg O_2/l	1140	848	1283

Tab.5. The results of series 5

Examinations	Unit	Waste water	Series 5	
			PIX - pH= 3 dose – 2.8 ml/l	Fenton's reagent 10 ml/l $FeSO_4$ – 20 % 2.5 ml/l H_2O_2 – 30 %
pH		10.08	3.10	3.90
Temperature	°C	20.7	20.5	21.1
Total phosphorus	mg P/l	16.2	0.86	3.77
COD	mg O_2/l	1664	1530	1506

Figure 2. The concentrations total phosphorus in wastewater, wastewater with PIX and wastewater with Fenton's reagent



When PIX was added to the waste water at pH =3, then the maximum removal efficiencies of total phosphorus were achieved. The results were irrespective to the initial concentrations of total phosphorus in the waste water.

Conclusions

The carried out experiments have shows the possibility of very high effects of phosphorus removal to level of few milligrams per liter, independent on the concentration of total phosphorus in the waste water. These results demonstrated, that addition PIX and/or Fenton's reagent permits very effective removal of total phosphorus. The best results would be obtained at low pH values.

References

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