Original Research

A Comparative Study of Metals Solubilization and Electrocoagulation Methods' Effectiveness in Orthophosphate Removal from Synthetic Wastewater

Izabela Wysocka*

Department of Environmental Engineering, Faculty of Environmental Sciences,
University of Warmia and Mazury in Olsztyn, Warszawska 117, 10-701 Olsztyn, Poland

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Abstract

A comparative study was carried out to evaluate the effectiveness of orthophosphate removal from wastewaters using two methods: electrocoagulation and metals solubilization. Both methods were found to enable orthophosphate removal with more than 90% effectiveness at relatively low concentration of orthophosphates in crude wastewaters. The method of metals solubilization is based on spontaneous corrosive processes occurring in wastewater. In contrast to electrocoagulation, its advantage is a lack of the necessity of applying voltage to solubilized electrodes (no consumption of electric current at this stage), while its drawback is the longer duration of the treatment process. This manuscript presents a comparative analysis of both these methods applied for the treatment of synthetic wastewaters with pH=3, pH=5, and pH=8. Depending on the type of wastewaters subject to the treatment process, the metals solubilization method may appear more justified economically, especially with both methods resuling in similar parameters of wastewaters after treatment.

Keywords: metals solubilization, electrocoagulation, wastewater treatment, orthophosphate removal

Introduction

Removal of biogenic compounds from wastewaters is commonly performed in the process of wastewater treatment. Removal is largely based on the application of biological methods. While removal of nitrogen compounds can be performed mainly through biological methods, the removal of phosphorus compounds very often needs to be supplemented with physicochemical methods [1]. Most frequently, these methods are based on the use of metal ions, e.g. Fe^{2+}, Fe^{3+}, Al^{3+}, or Ca^{2+}. Wastewaters are subject to coagulation processes with the addition of respective salts of these metals (conventional coagulation) or to electrocoagulation-based processes [2-6]. The latter are, however, relatively expensive due to electric energy consumption, but their advantage is a lack of the effect of sewage re-salinization [2-6].

The same advantage can be achieved when instead of the electrocoagulation process, metallic iron is used in the method of metals solubilization based on spontaneous corrosive phenomena [7-9].

In the case of the metals solubilization method, under anaerobic conditions the metal ions (e.g. iron) are introduced into a solution as a result of spontaneous corrosive processes that proceed according to Fig. 1 [3, 5, 6, 10, 11].

The method of electrocoagulation enhances those processes by increasing the rate of metal solubilization processes driven by voltage application to electrodes [12].

*e-mail: iwysocka@uwm.edu.pl

In both cases (electrocoagulation or metals solubilization method) the precipitation, agglomeration, or sorption methods will still be responsible for phosphorus removal from wastewaters, similarly as in the case of conventional coagulation [5-7, 10, 12-15].

This study is aimed at comparing the effectiveness of orthophosphate removal with electrocoagulation and metals solubilization methods, using steel electrodes and three types of wastewaters with different pH values (pH=3, pH=5, and pH=8).

Methods

The experiment was conducted at six research stations.

Three series of analyses were conducted according to the type of wastewater used.

Research Station Design

Each station included a glass container with a volume of 2,500 cm^3 and a magnetic stirrer (MS 11HS by WIGO company) with the stirring element in the form of a cylinder (ϕ 0.7 cm and length of 5 cm) (Fig. 3). Stirrer speed was 150 rpm.

Ten electrodes (5 from black steel and 5 from stainless steel, single electrode dimensions: 250×50×2 mm) were immersed into each station, and arranged alternately: black steel electrode – anode, and stainless steel electrode – cathode. Prior to use, the electrodes were exposed for 2 weeks to wastewater environment for activation (in order to form products of corrosion – iron oxides – on the surface of the electrodes). The activation of electrodes assures a more efficient course of the wastewater treatment processes [16].

The distance between the electrodes was 0.5 cm. The total surface of immersed parts of the electrodes reached 2,680 cm^2 per station.

The research stations were divided into two groups: the first included three stations in which the electrodes were bridged with a copper wire to facilitate the flow of electrons between the anode and the cathode, whereas the second group included the three stations in which each electrode was connected to direct current with the strength of 0.7 A per station, to obtain a current density of about 1 mA/cm^2. This current density was selected as optimal based on İrdemez et al. [5, 6].

In both cases, electrodes made of black steel served as anodes.

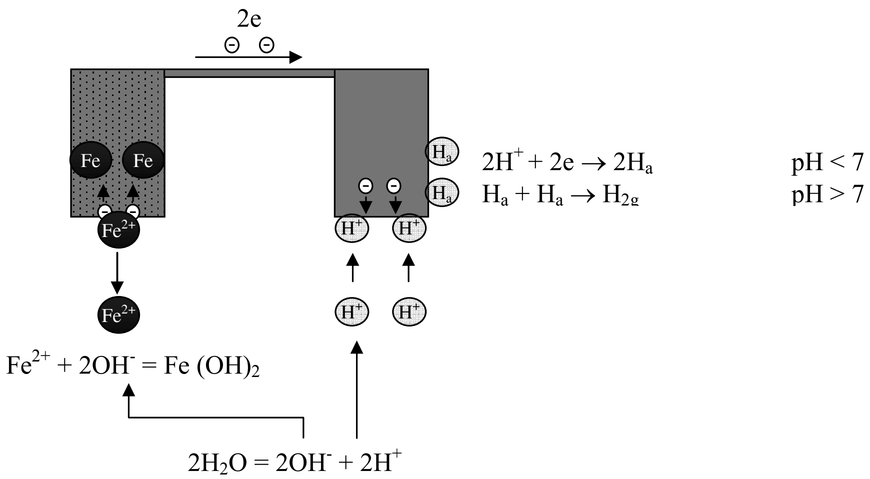

Fig. 1. Schematic of iron corrosion in oxygen-free aqueous solutions.

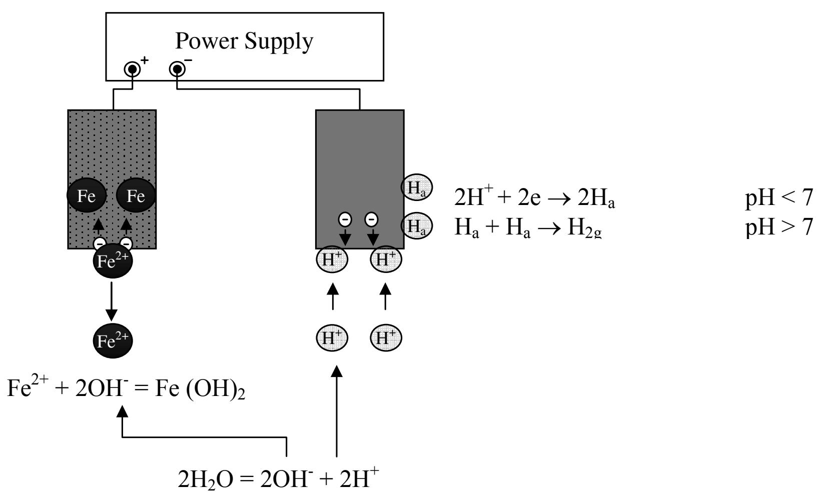

Fig. 2. Schematic of iron solubilization process in oxygen-free aqueous solutions with the use of direct current.

Table 1. Elemental composition of electrodes used in the study.

Type of steel/ type of electrode	Content [%]								
	C	Mn	P	Al	N	S	Si	Cr	Ni
Black steel/anode	0.130	0.52	0.011	0.043	0.006	0.005	-	-	-
Stainless steel/cathode	0.024	1.64	0.027	-	0.049	0.002	0.39	10.1	8.1

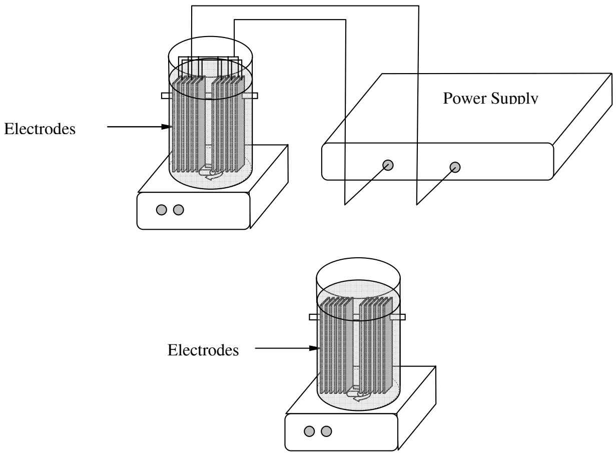

Fig. 3. Schematic of a research station. Source of direct current.

Type of Wastewaters Used in the Experiment

The experiment was conducted with three types of synthetic wastewaters differing in pH value (pH=3, pH=5, and pH=8). The desired concentration of orthophosphates was achieved by contaminating tap water with dipotassium phosphate (K_2HPO_4). The concentration of orthophosphates in prepared wastewaters reached 10.5 mg P/dm^3 (the wastewaters of pH 3 and 8) and 15.7 mg P/dm^3 (5 pH wastewater). The pH value of the wastewaters was controlled using a potassium hydroxide solution (KOH) and nitric acid (HNO_3). The wastewaters were prepared in a large tank, from which 2,500 cm^3 of wastewaters were collected for each research station.

Analytical Methods

Samples of wastewaters were collected directly from the research station after decanting. Afterward they were filtered through a paper filter of medium hardness.

The content of phosphorus in the samples examined was determined using the spectrophotometric method following measurement procedures provided by the manufacturer (ascorbic acid method).

The results were statistically characterized with the use of arithmetic mean and standard deviations. The advanced hypotheses, aimed at evaluating differences between particular elements, were verified with Student's *t*-test and analysis of variance. The differences were found to be significant at $p<0.05$.

Results and Discussion

A comparative study was conducted to evaluate the effectiveness of orthophosphate removal from synthetic wastewaters with two methods, namely: metals solubilization and electrocoagulation. The study was carried out for three pH values of synthetic wastewaters.

The analysis demonstrated that both methods, metals solubilization and electrocoagulation, resulted in a very high reduction in orthophosphate concentrations, exceeding 90% (Figs. 4-6), despite a low initial concentration of orthophosphates in the treated wastewaters (10.5 mg P/dm^3). At the final stage of the experiment, all types of treated wastewaters exhibit very low concentration of orthophosphates – from 0.69 to 0.00 mg P/dm^3. This indicates the feasibility of applying both compared methods for the removal of even residual concentrations of orthophosphates from wastewaters. The comparison of those methods demonstrated that electrocoagulation enabled faster orthophosphate removal when compared to the metals solubilization method (Figs. 4-6). The 90% reduction of orthophosphate concentrations (wastewater 3 pH and 8 pH – 1.0 mg P/ dm^3, and wastewater 5 pH – 1–6 mg P/ dm^3) was reached after approximately 150 min.

When applying the metals solubilization method to synthetic wastewater at pH=3, such an effectiveness of removal was achieved already after 270 min of wastewater contact with corroding steel electrodes (Fig. 4).

In comparison, during treatment of synthetic wastewaters with pH=8, the 90% reduction of orthophosphate removal (1.0 mg P/ dm^3) was reached already after 1,340 min (Fig. 5).

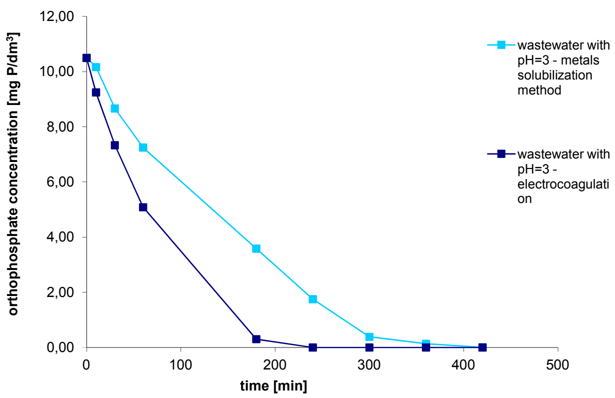

Fig. 4. Effectiveness of orthophosphate removal from wastewaters at pH=3 using the electrocoagulation and metals solubilization methods.

Similarly, in the case of wastewaters with pH=5, a 90% reduction of orthophosphates removal (1.6 mg P/ dm^3) was reached after 2,020 min (Fig. 6).

In the case of strongly acidic wastewaters the application of electrocoagulation may prove cost-ineffective and thus unjustified. The process of orthophosphate removal with that method from wastewaters with pH value around 3 yields comparable results to the method of metals solubilization.

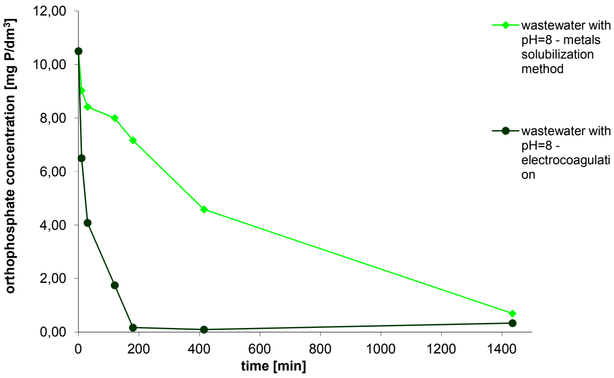

Fig. 5. Effectiveness of orthophosphate removal from wastewaters at pH=8 using the electrocoagulation and metals solubilization methods.

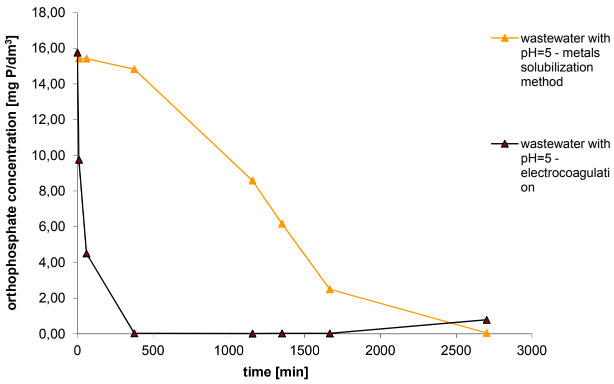

Fig. 6. Effectiveness of orthophosphate removal from wastewaters with pH=5 using the electrocoagulation and metals solubilization methods.

During treatment of less acidic wastewaters (pH of around 5) or basic wastewaters (pH of around 8), the effectiveness of both methods differs significantly in the initial phase of the experiment. The method of metals solubilization requires a longer contact time with corroding electrodes in order to assure similar levels of orthophosphate removal as achieved with the electrocoagulation method. However, owing to energy consumption of the electrocoagulation process (0.04 Wh/dm^3 of treated wastewaters), it may prove more cost-effective. The treatment of wastewaters with 90% effectiveness required energy consumption in the range of 0.11-0.15 W/dm^3.

Earlier works addressing the removal of phosphorus compounds from wastewaters [8, 9, 17] indicate the possibility of shortening the contact time at the expense of increasing the surface area of corroding electrodes.

Secondary contamination of wastewater with iron compounds also was observed during experiments (Fig. 7).

Literature studies suggest the presence of mainly iron oxides and hydroxides at +2 and +3 oxidation states (the presence of Fe^{+3} was probably due to the aeration of samples during mixing).

It is known from earlier studies [18, 19] that decanted wastewaters after the electrocoagulation process exhibit similar iron levels to those treated with metal digestion. Those methods introduce different amounts of iron to the solution, but the final concentration of soluble iron is limited by solubility and was similar in both samples [19]. On the contrary, suspended iron values were significantly different (Fig. 7). The electrocoagulation method introduces more iron to the solution [18], resulting in the higher amount of rusty precipitates in the wastewater.

It may be an indication of better utilization of iron ions in the metals digestion method and limitation of the problem of excessive sludge formation. It is going to be a subject of further studies.

The reported comparative study was focused on orthophosphates as the form of phosphorus being the most easily removable from wastewaters.

The achieved results seem to be promising enough to undertake a study into the effectiveness of removal of other forms of phosphorus.

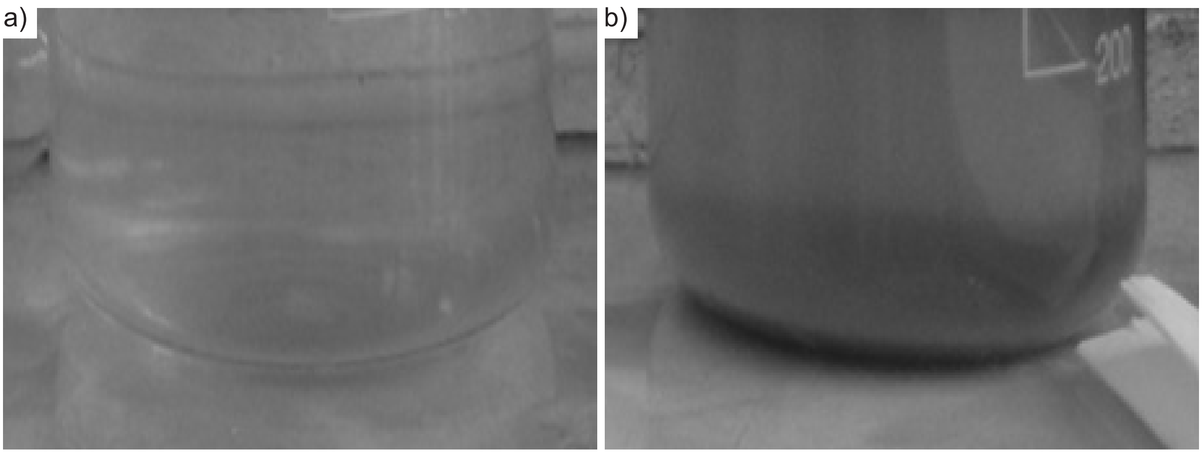

Fig. 7. Suspension in sewage treated with the metal solubilization method (a) and electrocoagulation method (b).

Conclusions

The methods of electrocoagulation and metals solubilization enable very efficient orthophosphate removal from wastewaters. In spite of the fact that the wastewaters used in the study were characterized by a relatively low initial concentration of orthophosphates (ca. 10 mg P/dm^3), both methods allowed to reached more than 90% removal effectiveness (3 pH and 8 pH wastewaters – 1.0 mg P/ dm^3, 5 pH wastewater – 1.6 mg P/dm^3) of the treatment process. The method of electrocoagulation (with the same surface area of electrodes) enables a significantly faster treatment process, but it is energy-consuming. Depending on the type of wastewaters to be treated, the method of metals solubilization may be more cost-effective. Wastewaters with pH=3 treated with the metals solubilization method required extending the contact time only by 120 min. The contact time of wastewaters with corroding electrodes may be shortened by increasing the surface area of electrodes, which has already been determined in earlier studies.

The methods differ with regard to the amount of iron remaining in the sewage in a suspended form. This indicates a better use of iron ions in the metal digestion method and it slightly limits the problem of an excessive amount of sludge.

In turn, in the case of wastewaters with pH of approximately 5, achieving 90% reduction (1.6 mg P/dm^3) required extending the contact time by 1,900 min. In this case, however, the application of a metals solubilization method may appear too difficult.

References

1. PAK D., CHANG W. Simultaneous removal of nitrogen and phosphorus in a two-biofilter system. Water Sci. Technol. **41**, 12, 101, **2000**.
2. BUZZINIA A.P., PATRIZZIA L.J., MOTHEOB A.J., PIRESA E.C. Preliminary evaluation of the electrochemical and chemical coagulation processes in the post-treatment of effluent from an upflow anaerobic sludge blanket (UASB) reactor. J. Environ. Manage. **85**, 847, **2007**.
3. ŞENGIL A., ÖZACAR M. Treatment of dairy wastewaters by electrocoagulation using mild steel electrodes. J. Hazard. Mater. **B137**, 1197, **2006**.
4. BEKTAS N., AKBULUT H., INAN H., DIMOGLO A. Removal of phosphate from aqueous solutions by electrocoagulation. J. Hazard. Mater. **106B**, 101, **2004**.
5. İRDEMEZ Ş., DEMIRCIOĞLU N., YILDIZ Y.Ş., BINGÜL Z. The effects of current density and phosphate concentration on phosphate removal from wastewater by electrocoagulation using aluminum and iron plate electrodes. Separ. Purif. Technol. **52**, 218, **2006**.
6. İRDEMEZ Ş., DEMIRCIOĞLU N., YILDIZ Y.Ş. The effects of pH on phosphate removal from wastewater by electrocoagulation with iron plate electrodes. J. Hazard. Mater. **B137**, 1231, **2006**.
7. HUANG Y. H., HANG T. C. Effects of dissolved oxygen on formation of corrosion products and concomitant oxygen and nitrate reduction in zero-valent iron systems with or without aqueous Fe^{2+}. Water Res. **39**, 1751, **2005**.
8. WYSOCKA I. Applying Corrosion Processes for Phosphorus Compound Removal in Sewages. The Conference Proceedings, 2nd IWA Specialized Conference, Nutrient management in wastewater treatment processes, Kraków, Poland, 6-9 September 2009, pp. 939-946, **2009**.
9. WYSOCKA I., GIZA M.N. Comparison of the results of removing orthophosphates from sewage using the electrocoagulation method and the metal digestion method., Rocz. Ochr. Sr. **13**, 1915, **2011** [In Polish].
10. BAYRAMOGLU M., KOBYA M., CAN O. T., SOZBIR M. Operating cost analysis of electrocoagulation of textile dye wastewater. Separ. Purif. Technol. **37**, 117, **2004**.
11. CHEN G. Electrochemical technologies in wastewater treatment. Separ. Purif. Technol. **38**, 11, **2004**.
12. NOUBACTEP C., SCHÖNERB A. Metallic iron for environmental remediation: Learning from electrocoagulation. J. Hazard. Mater. **175**, 1075, **2010**.
13. ÜN Ü. T., KOPARAL A. S., ÖĞÜTVERENB Ü. B. Hybrid processes for the treatment of cattle-slaughterhouse wastewater using aluminum and iron electrodes. J. Hazard. Mater. **164**, 580, **2009**.
14. KUMAR M., PONSELVAN F. I. A., MALVIYA J. R., SRIVASTAVA V. CH., MALL I. D. Treatment of bio-digester effluent by electrocoagulation using iron electrodes. J. Hazard. Mater. **165**, 345, **2009**.
15. DUAN J., GREGORY J. Coagulation by hydrolysing metal salts. Adv. Colloid Interfac. **100-102**, 475, **2003**.
16. HUTNAN M., DRTIL M., KALINA A. Anaerobic stabilisation of sludge produced during municipal wastewater treatment by electrocoagulation. J. Hazard. Mater. **B131**, 163, **2008**.
17. WYSOCKA I., KRZEMIENIEWSKI M., JANCZUKOWICZ W., PESTA J. Influence of metal ions introduction to the solution by corrosion, on phosphorus removal from wastewater. Natural Sciences **9**, 307, **2003**.
18. MOLLAH M.Y.A., SCHENNACH R., PARGA J.R., COCKE D.L. Elactrocoagulation (EC) – science and applications. J. Hazard. Mater., **B84**, 29, **2001**.
19. WYSOCKA I., KRZEMIENIEWSKI M. The influence of the metal dissolution process on the final effect of phosphorus compounds removal from treated sewage, Pol. J. Environ. Stud., **17**, (3A), 596, **2008**.