
The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM)

Volume 1, Pages 339-346

ICONTES2017: International Conference on Technology, Engineering and Science

DDT REMOVAL BY NANO ZERO VALENT IRON: INFLUENCE OF pH ON REMOVAL MECHANISM

Kubra Altuntas
Yildiz Technical University

Eyup Debik
Yildiz Technical University

Abstract: Persistent organic compounds are resistant to biological degradation and can be transported long distances by releasing into the atmosphere and can be found in the atmosphere for a long time. DDT is one of the persistent organic compounds which is prohibited by Stockholm Convention. Against the prohibition in many countries, DDT, which is still in limited use in undeveloped countries, has a very low carcinogenic concentration (0,23 µg/L). It is stated in the literature that nanomaterials have been used effectively in the last decades for the removal of environmental pollutants. In this study, the mechanism of removal by nano zero valent iron was investigated by researching the pH effect at low DDT concentration. pH and ORP changes after treatment were investigated. Almost total DDT was removed within 5 minutes and pH effect on removal mechanism has found to be negligible. The ORP values decreased rapidly during the first minutes of the study. In addition, the effluent Fe²⁺ concentrations were also investigated and these results showed that oxidation was effective in the removal mechanism.

Keywords: DDT, nZVI, removal mechanism, ORP

Introduction

Pesticide residues are commonly found in soil, atmospheres and water resources worldwide, as a result of the use of pesticides in agriculture. Although pesticides have been seen as life-saving products in the past, they have been shown to have significant toxic effects on humans and other living organisms in recent years. Particularly organochlorine pesticides; it has been found that microorganisms affect all living things in the food chain from humans to humans due to their accumulation in oil and their persistence. These pesticide residues, which are resistant to biological degradation, can be transported in long distances by release in the atmosphere and can be found in the atmosphere for a long time. Among the persistent organic pollutants, the most researched pesticide, DDT and its derivatives have been used since 1940s against diseases such as malaria, typhus. The various agricultural products were sprayed on the cotton, especially as an agricultural pesticide. Although its use is banned in many countries, widespread usage means that DDT residues can be found everywhere. Under the Stockholm Convention, DDT is restricted that it can only be used for the control of disease viruses and is listed in Annex B.

Pesticides are highly toxic and non-biodegradable because of have boundaries difficult to disassemble. There are many methods of treatment that have been investigated for the removal of pesticides. There are investigations on the treatment of pesticide water with chemical oxidation (Ormad *et al.* 2008), electrochemical treatment (Muff *et al.* 2009), chemical treatment and biological treatment of activated sludge systems (Lafi & Al-Qodah 2006; Li *et al.* 2010), adsorption (Gupta & Ali 2008; Humbert *et al.* 2008) and membrane treatment systems (Sarkar *et al.* 2007). Advanced oxidation processes that oxidize pollutants by forming hydroxyl radicals are the most studied topics on the treatment of pesticides (Lin & Lin 2007; Sarkar *et al.* 2007; Samet *et al.* 2010; Sanches *et al.* 2010; Yahiaoui *et al.* 2011)

- This is an Open Access article distributed under the terms of the Creative Commons Attribution-Noncommercial 4.0 Unported License, permitting all non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

- Selection and peer-review under responsibility of the Organizing Committee of the conference

*Corresponding author: Kubra Altuntas-E-mail: kulucan@yildiz.edu.tr

Nanoparticles have more surface area and porosity than conventional adsorbents. As an alternative to adsorption processes, the use of nanoparticles capable of both adsorption and fenton-like reactions, for environmental pollution control is generally based on soil pollution studies, but studies on water pollution in recent years have begun to increase, and the use of nanoparticles are globally significance. The most common of these nanoparticles are carbon nanotubes, titanium oxide and nano-zero valent iron. There are studies on the degradation of organic compounds such as chlorinated organic solvents, organochlorine pesticides and polychlorinated biphenyls which will become one of the important research topics in the world.

DDT is low soluble in water (0,23mg/L (James Pontolillo & Eganhouse 2001)) and DDT cancerogenic concentration level is 0,23 µg/L according to EPA's Regional Screening Levels Table (EPA 2017). In the light of these data, removal at low concentration of DDT is examined using nZVI in present study. Removal is examined by considering effect of pH and removal mechanism is also presented.

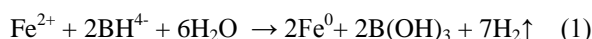
Materials and Methods

Chemicals

p,p' DDT and internal standard (Decachlorobiphenyl & TCMX) were purchased from Accu Standards. Solid phase extraction (SPE) was performed by C-18 Catridges which were ordered from Thermo Scientific-Dionex™ SolEx™ C18. FeSO₄·7H₂O and NaBH₄ used in nano zero valent iron (nZVI) synthesis were ordered from Merck. Sodium sulfate used in column analysis was also purchased from Merck, and dried at 150°C for 2h before use. Water used in entire study including SPE method was ultrapure.

Synthesis of nZVI Nanoparticles

nZVI was synthesized using borohydride method, as performed in the reaction given below (Eq (1)).



FeSO₄·7H₂O solution concentration was 0,03M and dissolved in water:ethanol mixture. In order to inhibit the reaction of the produced hydrogen with the iron nanoparticles during the reaction 1ml of 0,5M NaOH and to prevent aggregation 0,5 g PEG was added to solution. Borohydride solution was added with rate of 15 mL/min to iron sulfate solution by peristaltic pump. After obtaining nanoparticle, mixture was wash with ethanol and pure water in order to inhibit negative effects of SO₄²⁻ and Br⁻ ions. Nanoparticles were stored in ethanol and, before experiments it is dried at 50°C. Particle size of nZVI was measured as 88 nm by zeta sizer. isoelectric point of synthesized nZVI is determined as pH 7.8 as given in Figure 1.

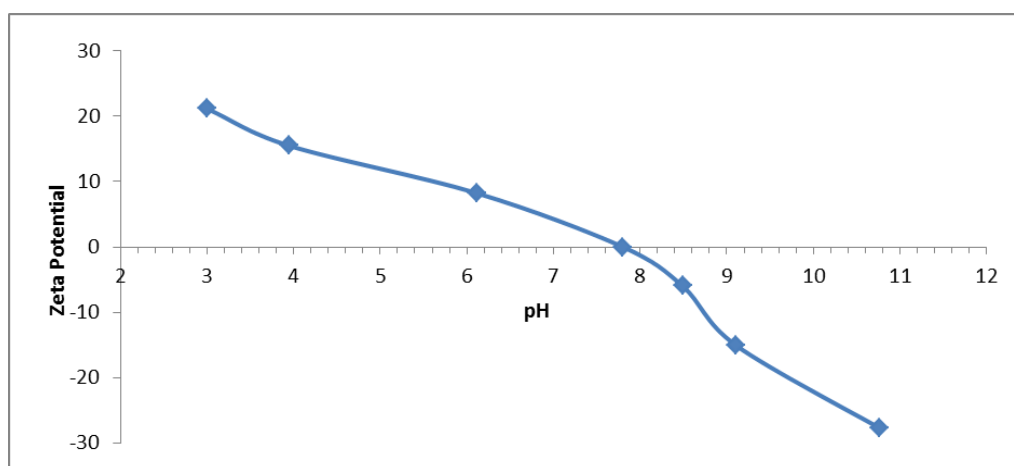


Figure 1. Isoelectric point of nZVI

DDT Degradation Experiments

Synthetic solution of DDT is prepared by DDT stock solution prepared in methanol (5µg/L). Experiments were conducted at amber glass bottles with teflon caps in vertical shaker placed in incubator (20°C) under aerobic

conditions. Sample volume was 50 ml and each individual samples were containing 0.2g/L nZVI concentration with 5µg/L DDT concentration. NaOH and HCl (Merck Qaulity) was also used in investigation of pH effect.

Analysis

Gas chromatography equipped with ECD detector (Perkin Elmer Clarus 500) was used in DDT determination. Because of detection limit is higher than 0.5 mg/L, all samples were concentrated by SPE. For appropriate method of SPE recovery studies were conducted. After SPE, each sample was passed through a glass column containing 2.5 gr anhydrous sodium sulfate (Na_2SO_4) in order to keep water. Before and after sample extraction at glass column, 5 ml of methanol was used. Before adjusting volume to 1 ml with nitrogen gas, internal standard (TMCX) was added.

Fe was analysed at atomic adsorption spectrometer (Perkin Elmer AAnalyst 400 Atomic Absorption Spectrometer). The system pH and ORP was followed before and after each experiment. pH and ORP Analysis was determined by pH/ORP sensor (WTW Multi 9630 IDS).

Results aand Discussion

SPE Method Determination For DDT

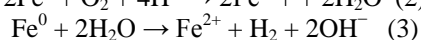
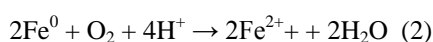
The SPE method has been developed inspired by the work of Kouzayha et al (Kouzayha *et al.* 2012). For conditioning and elution applications, methanol and ultrapure water was used. Table 1 shows the conditions which conditioning, drying, filtration and elution have been applied. Recoveries were also calculated and presented in Table 1. The most appropriate SPE method was selected as Method 8 by having recovery higher than 99%.

Table 1. SPE method determination

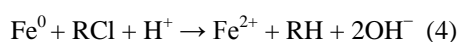
Applications	SPE Method 1	SPE Method 2	SPE Method 3	SPE Method 4	SPE Method 5	SPE Method 6	SPE Method 7	SPE Method 8
Conditioning	10ml MeOH	10ml MeOH	10ml MeOH	10ml MeOH	10ml MeOH	3ml MeOH	3ml MeOH	3ml MeOH
	10ml Water	10ml Water	10ml. Water	10ml Water	20ml Water	3ml Water	3ml Water	3ml Water
Drying	No	No	5 min	5 min	No	No	No	No
Percolation	500 µL	500 µL	500 µL	500 µL	500 µL	500 µL	500 µL	500 µL
Washing	10ml Water	10ml Water	10ml Water	10ml Water	10ml Water	10ml Water	10ml Water	10ml Water
Drying	No	5 min	5 min	10 min	5 min	10 min	5 min	2 min
Elution	10ml MeOH	10ml MeOH	10ml MeOH	10ml MeOH	10ml MeOH	10ml MeOH	10ml MeOH	10ml MeOH
DDT Recoveries	20.54 %	58.03 %	41.48 %	37.69 %	21.81 %	81.86 %	95.74 %	99.01 %

Effect of pH on DDT removal and removal mechanism

Initial and final pH and ORP of the system was investigated. It was observed that effluent pH in low initial pH experiments were changed towards to pH 8 (Figure 2). In the experiments with low initial pH, pH was increased. This can be explained as nZVI oxidation in which the reaction of water and oxygen(Sayles et al. 1997) according to Equation (2) and Equation (3).



In addition, compounds with chlorine in the presence of water are giving reaction with H^+ in the dechlorination process (Eq. (4))(Sayles et al. 1997).



Because of rapid corrosion of nZVI in low initial pH, hydroxide ion concentration increases the pH rapidly (Wu et al. 2017).

The effluent DDT concentrations at different initial pHs are shown in Figure 3. It can be said that >98% of DDT is eliminated in very limited time as 5 minutes. According to results, different initial pHs were not affected noticeably to DDT removal at low concentrations.

DDD and DDE, the metabolites of DDT, were also investigated and shown in Figure 3. According to the proposed dechlorination process, oxidation of DDT results in the formation of DDD, and DDE is formed by oxidation of DDD. In 5 minutes of reaction time, DDD formation was determined for all pH values. In addition, ORP changes indicate that the majority of the oxidation takes place in the first 5 minutes (Figure 4). It was also observed that the DDD concentration detected at low pH (pH 2) was lower than higher pH values. It can be said that approximately 1% of DDT is oxidized to DDD at pH 4, 6.5 and pH 10. After 60 minute of reaction time, DDE formation was observed and the concentration was found to be very low (4 ng / L for pH 6.5).

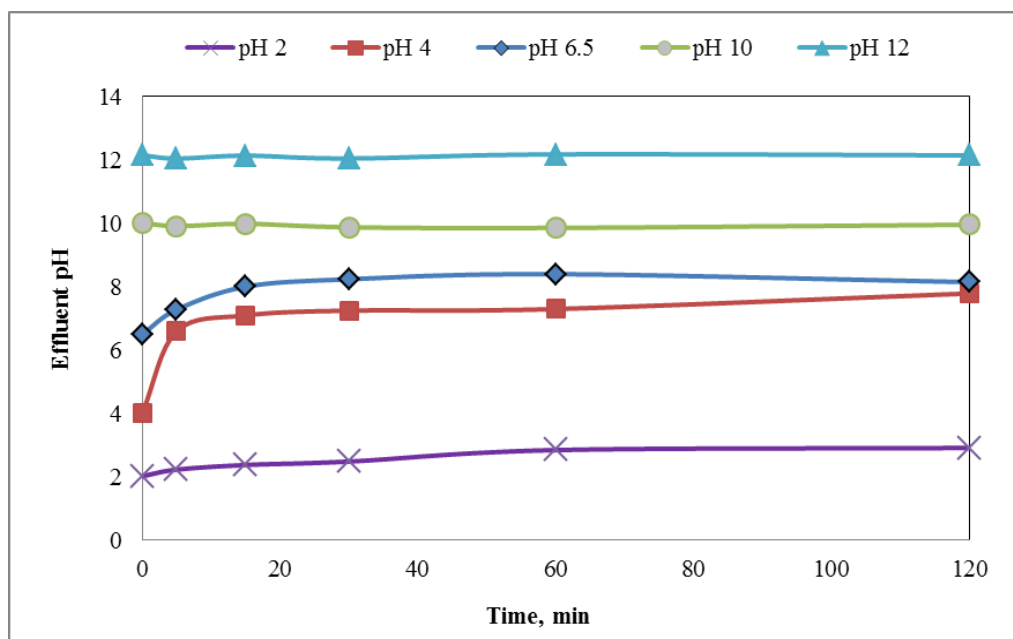


Figure 2. pH change at different pH

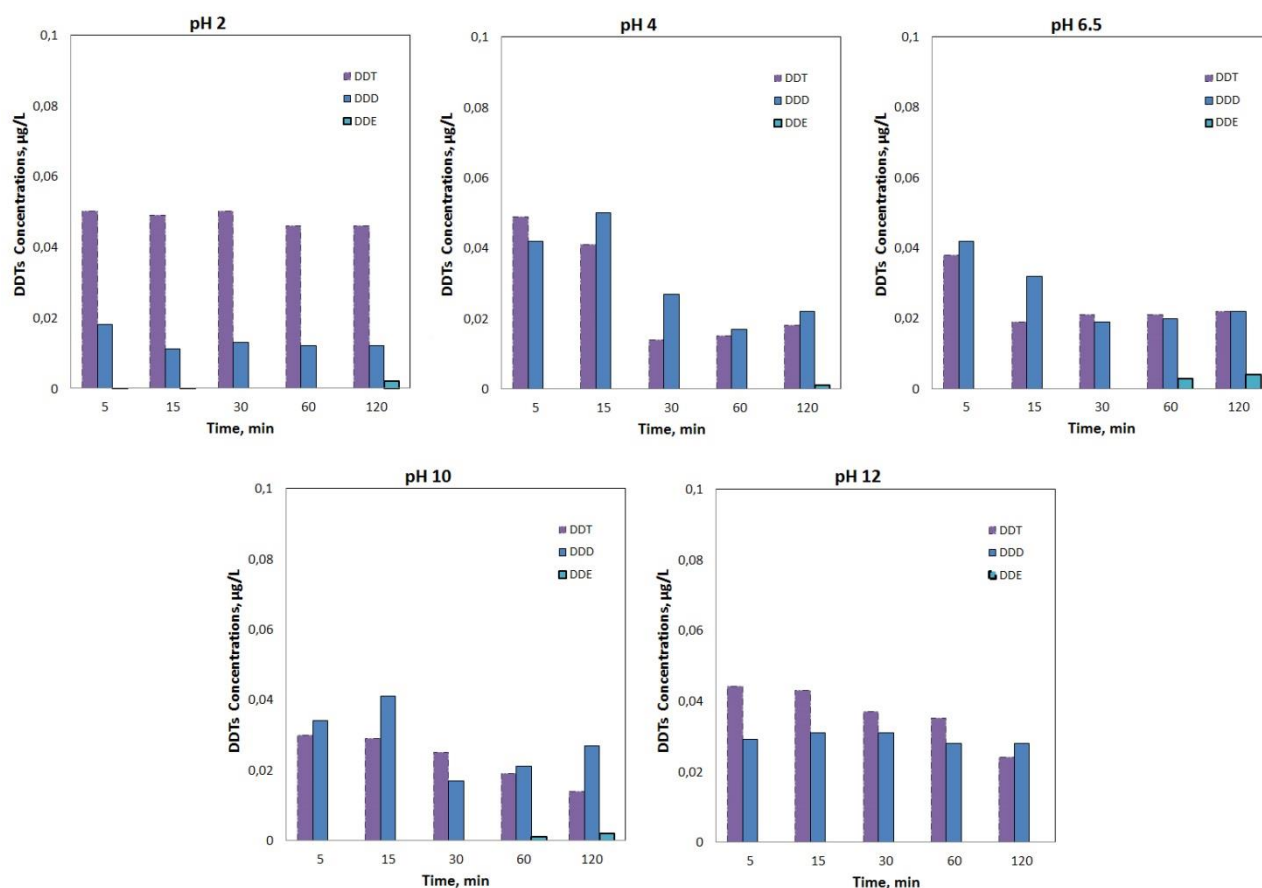


Figure 3. DDT and metabolites concentration after treatment with nZVI

According to the DDD and DDE concentrations formed, it can be said that the removal is not achieved only by oxidation. The correlation coefficients for Langmuir and Frunlich, which are the most commonly used isotherms for adsorption process, have been calculated and are given in Table 2. It can be said that both isotherms are suitable because the correlation coefficients obtained for all initial pH studies are very close to each other. Maximum adsorption capacity calculations from Langmuir isotherm are also given in Table 1. The results are also so similar, but the maximum adsorption capacity was obtained at pH 6.5.

Table 2. Correlation coefficients of isotherms and q_{\max} coefficient for Langmuir isotherm

Isotherm	pH 2	pH 4	pH 6.5	pH 10	pH 12
Langmuir	0.784	0.9999	0.999	0.993	0.976
Freundlich	0.804	0.9999	0.998	0.996	0.987
q_{\max}	14.27	23.38	23.71	22.26	20.12

During the study ORP changes were observed and shown in Figure 4. According to Equation 2 and Equation 3, while effluent pH was increasing, oxidation reduction potential should be decrease. Similarly, a rapid decrease in ORP values was observed at all pH values in 5 minutes. For the results in 5 minutes, as the initial pH increases, the ORP difference was reduced. The highest ORP change was obtained at pH 2 as 370 mV and the lowest ORP change was obtained at pH 10 as 110 mV.

ORP difference during reaction time has shown similar characteristic for all initial pH values. ORP decreased quickly and then approaches to a value near zero point within 60 minutes. The lowest ORP was obtained with original pH at 30 minute of reaction time.

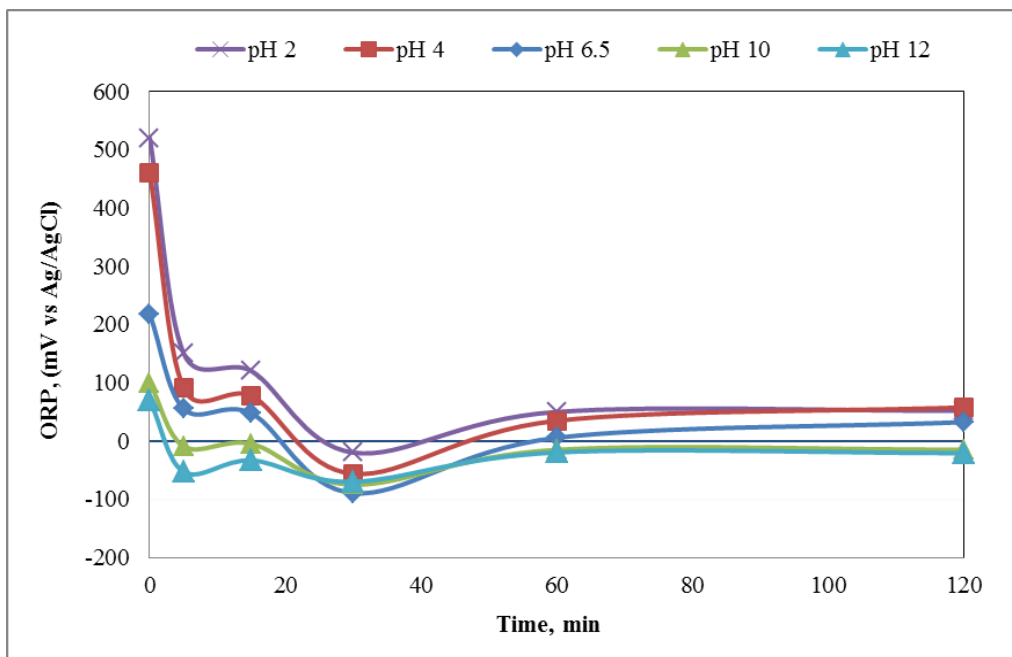


Figure 4. ORP change in degradation of DDT at different initial pH

In order to understand the effect of pH on corrosion of nZVI, point of zero charge (pH_{pzc}) and effluent Fe^{2+} concentration were determined after corrosion with varying initial pH (2, 4, 7, 10 and 12) and is shown in Figure 5 and Figure 6, respectively.

For all samples, zeta potential at pH values lower than pH 7 were positive, and pH values higher than pH 9 were negative. Original pH_{pzc} of nZVI was 7.8 and pH_{pzc} of nZVI after corrosion at pH 2, 4, 7, 10 and 12 is 8.2, 8.2, 7.9, 7.9 and 8.0 respectively. For all pH values pH_{pzc} was higher than original pH_{pzc} of nZVI. pH_{pzc} of iron hydroxides is ranging pH 7 – 9 (Wu *et al.* 2017), consequently, difference on pH_{pzc} after corrosion showed that different corrosion products (ferrous compounds) on nZVI surface were formed (Wu *et al.* 2017),.

In order to show corrosion, Fe concentrations after treatment were researched. In previous study (Zhang *et al.* 2015) it is reported that low initial pH is leading to excessive corrosion of nZVI. Similarly, corrosion of nZVI with low pH can be seen in

Figure 6. The highest corrosion was found at pH 2. As the pH value increased, the corrosion on nZVI decreased.

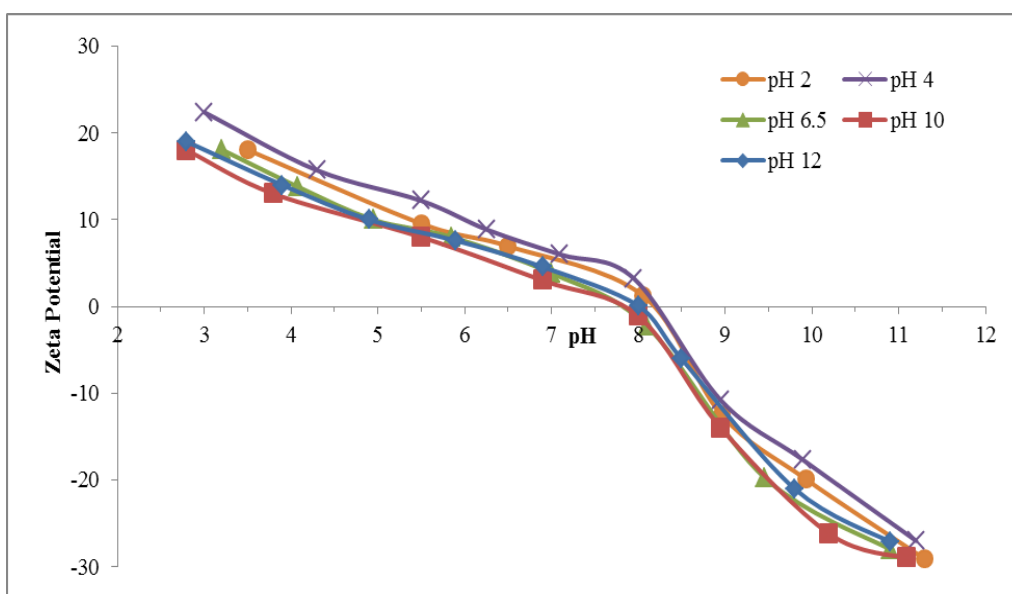


Figure 5. Point of zero charge difference at different initial pH

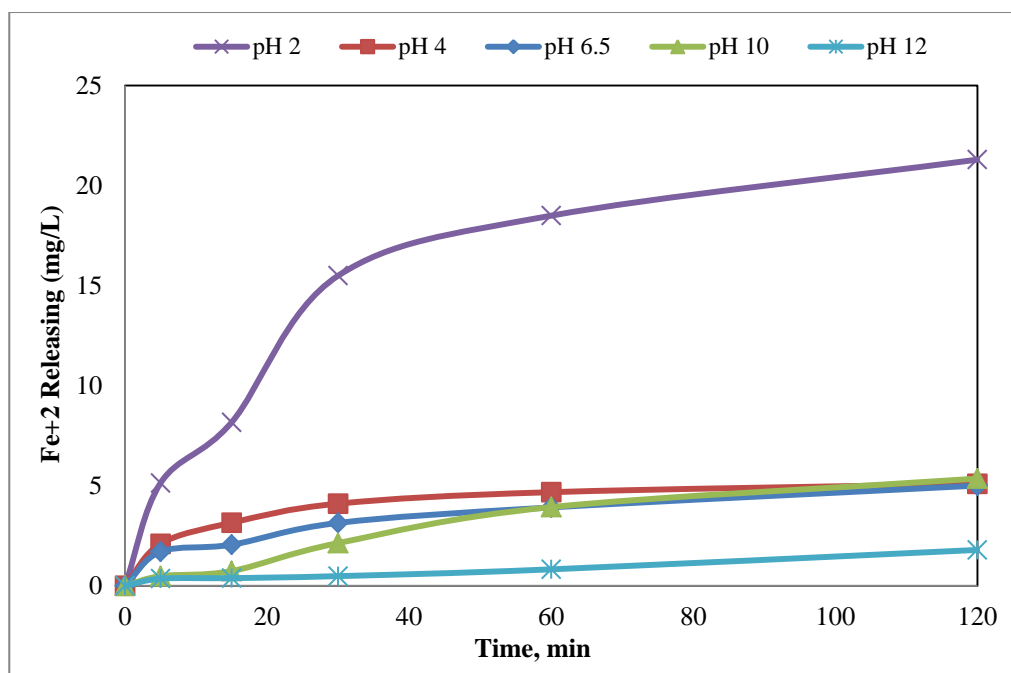


Figure 6. Fe Releasing at different initial pH

Conclusion

Although the effect of varied pH on DDT removal at low concentration was negligible, effect on the corrosion of nZVI was found to be high when Fe^{2+} formation was investigated. In addition to Fe^{2+} formation, ORP decrement and DDT metabolites formation are the allegement for oxidation process. DDT in all initial pH was almost totally removed (>98% of removal rate). While DDD is formed in the first minutes of study, DDE is formed only after 60 minutes of reaction time. The pH effect was negligible when removal efficiencies are compared, but with the adsorption isotherms investigation, the calculated maximum adsorption capacity was found to be higher at around pH 6.5.

Acknowledgement

This work was supported by Scientific Research Projects of Yildiz Technical University (BAP – DOP Project No: 2015-05-02-DOP02). We also thank M. Iberia Aydin for his help on zeta potential analysis.

References

- EPA (2017). Regional Screening Levels (RSLs) - Generic Tables (June 2017). In.
- Gupta V. K. and Ali I. (2008). Removal of endosulfan and methoxychlor from water on carbon slurry. *Environmental Science & Technology* 42(3), 766-70.
- Humbert H., Gallard H., Suty H. and Croue J. P. (2008). Natural organic matter (NOM) and pesticides removal using a combination of ion exchange resin and powdered activated carbon (PAC). *Water Res* 42(6-7), 1635-43.
- James Pontolillo and Eganhouse R. P. (2001). The Search for Reliable Aqueous Solubility (S_w) and Octanol-Water Partition Coefficient (K_{ow}) Data for Hydrophobic Organic Compounds: DDT and DDE as a Case Study. *U.S. Geological Survey Water-Resources Investigations Report 01-4201*.
- Kouzayha A., Rahman Rabaa A., Al Iskandarani M., Beh D., Budzinski H. and Jaber F. (2012). Multiresidue Method for Determination of 67 Pesticides in Water Samples Using Solid-Phase Extraction with Centrifugation and Gas Chromatography-Mass Spectrometry. *American Journal of Analytical Chemistry* 03(03), 257-65.
- Lafi W. K. and Al-Qodah Z. (2006). Combined advanced oxidation and biological treatment processes for the removal of pesticides from aqueous solutions. *J Hazard Mater* 137(1), 489-97.

- Li F. B., Li X. M., Zhou S. G., Zhuang L., Cao F., Huang D. Y., Xu W., Liu T. X. and Feng C. H. (2010). Enhanced reductive dechlorination of DDT in an anaerobic system of dissimilatory iron-reducing bacteria and iron oxide. *Environ Pollut* 158(5), 1733-40.
- Lin C. and Lin K. S. (2007). Photocatalytic oxidation of toxic organohalides with TiO₂/UV: The effects of humic substances and organic mixtures. *Chemosphere* 66(10), 1872-7.
- Muff J., Andersen C. D., Erichsen R. and Soegaard E. G. (2009). Electrochemical treatment of drainage water from toxic dump of pesticides and degradation products. *Electrochimica Acta* 54(7), 2062-8.
- Ormad M. P., Miguel N., Claver A., Matesanz J. M. and Ovelleiro J. L. (2008). Pesticides removal in the process of drinking water production. *Chemosphere* 71(1), 97-106.
- Samet Y., Agengui L. and Abdelhédi R. (2010). Electrochemical degradation of chlorpyrifos pesticide in aqueous solutions by anodic oxidation at boron-doped diamond electrodes. *Chemical Engineering Journal* 161(1-2), 167-72.
- Sanches S., Barreto Crespo M. T. and Pereira V. J. (2010). Drinking water treatment of priority pesticides using low pressure UV photolysis and advanced oxidation processes. *Water Res* 44(6), 1809-18.
- Sarkar B., Venkateshwarlu N., Nageswara Rao R., Bhattacharjee C. and Kale V. (2007). Potable water production from pesticide contaminated surface water—A membrane based approach. *Desalination* 204(1-3), 368-73.
- Sayles G. D., You G. R., Wang M. X. and Kupferle M. J. (1997). DDT, DDD, and DDE dechlorination by zero-valent iron. *Environmental Science & Technology* 31(12), 3448-54.
- Wu C., Tu J. W., Liu W. Z., Zhang J., Chu S. Q., Lu G. N., Lin Z. and Dang Z. (2017). The double influence mechanism of pH on arsenic removal by nano zero valent iron: electrostatic interactions and the corrosion of Fe-0. *Environmental Science-Nano* 4(7), 1544-52.
- Yahiaoui O., Aizel L., Lounici H., Drouiche N., Goosen M. F. A., Pauss A. and Mameri N. (2011). Evaluating removal of metribuzin pesticide from contaminated groundwater using an electrochemical reactor combined with ultraviolet oxidation. *Desalination* 270(1-3), 84-9.
- Zhang Y. L., Chen W., Dai C. M., Zhou C. L. and Zhou X. F. (2015). Structural Evolution of Nanoscale Zero-Valent Iron (nZVI) in Anoxic Co²⁺ Solution: Interactional Performance and Mechanism. *Scientific Reports* 5.