

Removal of phosphate ions and Pb (II) from synthetic water matrices using “green” synthesized zero valent iron

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Abstract

In this paper, phosphates and lead were chosen as the priority pollutant, because their increased concentrations in water can be caused by the release of various untreated effluents and thus can cause serious damage to the environment. Nano zero valent iron synthesized by leaves, In addition to being considered an environmentally friendly method, it is a stable and efficient material. The influence of process conditions was examined by applying a statistical model of the new generation - definitive screening design, which played a significant role in the optimization of the entire experiment. The influence of 4 process parameters on the efficiency of lead removal was examined: initial phosphate concentration (from 1 mgL⁻¹ to 9 mgL⁻¹) initial lead concentration (from 1 mgL⁻¹ to 9 mgL⁻¹), dose of nZVI (from 2 mL to 16 mL) and pH value (from 2 to 10). Under optimal conditions, the dose of nZVI 9 mL, 8.76 mgL⁻¹, phosphate concentration 2 mgL⁻¹ and pH value 3 the removal efficiency is 99.41%. Based on the verification and confidence interval, the adopted model was found to be appropriate and to describe well the process of removing phosphate in the presence of lead from the synthetic aqueous matrix.

Keywords: oak-nZVI, Lead, Phosphorus, statistical model

1. Introduction

Unfortunately, rapid industrial development and changes in other human activities have led to a worldwide increase in the levels of phosphorus (P) entering rivers, lakes and coastal waters, which has directly led to increased incidents of eutrophication and the frequency of toxic algal blooms (Xu *et al.*, 2020). Similar concern is lead (Pb) which is a highly toxic non-biodegradability and environmentally persistent contaminant (Li *et al.*, 2018). In particular the dual contaminant of environments with both heavy metals and ion has attracted worldwide attention because the toxicity of both contaminants can be amplified

resulting in increased accumulation in food webs, leading to increased rates of diseases.

Of all the current environmental remediation technologies, adsorption the most advantageous because it is economical, consumes only small amounts of energy and is relatively easy to practically implement (Xu *et al.*, 2020). Zero valent iron nanoparticles in an aqueous medium react with water and oxygen to form an outer layer of iron (hydr) oxide, which reacts as an effective adsorbent for potentially toxic metals. The usage of plant leaves to generate nanoparticles is based on the reduction of ferric or ferrous iron to zero valent iron (Fe⁰) using biologically-active substances from plant extracts. In addition to the reduction of Fe²⁺/Fe³⁺, polyphenols, flavonoids and other reducing substances effectively prevent nanoparticles from agglomeration, and cap the metal protecting it from oxidation (Kecić *et al.*, 2018).

In laboratory test conditions, one of the important conditions for the adsorption of metals from water is the appropriate ratio of nZVI dose and metal/ion concentration. Definitive screening design (DSD) model used for experiment design. The principle of the DSD statistical method is based on the application of a numerical algorithm that maximizes the determinant of the matrix of the main effect model. The analysis conceived in this way is used to determine the optimal conditions, significant factors, as well as their two-factor interactions. The advantage of applying DSD analysis is the reduced number of performed experiments with maximum precision (Kecić *et al.*, 2018).

The aim of this paper is based on the investigation of the application of nano-zero valence iron synthesized using oak leaves to remove lead and phosphate from a synthetic aqueous matrix. Using DSD analyzes, the influences of process parameters were examined: nZVI dose, phosphate concentration, lead concentration and pH value. Optimization of the entire process has also been done.

2. Materials and Methods

Nano-zero valent iron is synthesized using oak leaves extract as a reducing agent according to *Sljepčević et al., 2021*. DSD was used to investigate the influence of four operating variables in the process: initial concentration lead (1 - 9 mgL⁻¹), initial phosphate ion concentration (1 - 9 mgL⁻¹), oak-nZVI dosage (2 - 16 mL), and pH value (2-10). Experiments were performed for lead and phosphate mixture with a final mixture volume of 100 mL. After the adjustment of the appropriate pH value (2, 6, 10) with 0.1M HNO₃ and 0.1M NaOH solution, sample bottles were placed on a shaker at 180 rpm, for 60 min at a constant room temperature of 23°C. After shaking, the solutions were centrifuged at 4000 rpm for 12 minutes and filtered on a 0.22 µm filter. Residual phosphate concentrations were determined according to SRPS EN ISO 6878:2008 method. Residual concentrations of Pb²⁺ were determined by inductively coupled plasma with mass spectrometry (ICP-MS, Agilent Technologies 7700 Series).

3. Results and discussion

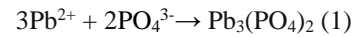
The results of simultaneous removal of phosphate and lead from the synthetic aqueous matrix indicated that removal efficiency is in the range of 10.22% to 100% for phosphates and 31.74% to 98.09% for lead. The coefficient of determination for the removal of phosphate is lower ($R^2 = 0.709$) in the respective to ($R^2 = 0.878$) for the lead. Factors of statistical importance for phosphate removal are shown by the bold values in Table 1. Significant factors for phosphate removal are 3 two-factor interactions, between lead concentration and pH value, nZVI dose and phosphate concentration and phosphate concentration and pH value, while lead concentration also occurs as a single significant factor.

Table 1. Estimated regression coefficients

Parameter	Estimate value	Std Error	t ratio	Prob> F
Lead (mgL⁻¹)*pH	-25.157	4.440	-5.670	<0.0001*
Lead (mgL⁻¹)	12.098	3.076	3.930	0.0008*
Oak-nZVI (mL)*Phosphate (mgL⁻¹)	-13.763	4.440	-3.100	0.0056*
Phosphate (mgL⁻¹)*pH	8.688	3.971	2.190	0.0407*
pH	-2.687	3.076	-0.870	0.3927
nZVI (mL)	0.954	3.076	0.310	0.7597
Phosphate (mgL⁻¹)	0.6395	3.076	0.210	0.8374

Although the pH value is not statistically significant as a single factor, it nevertheless builds 2 two-factor interactions with lead concentration and phosphate concentration in the phosphate removal process in the presence of lead (Figures 1a and 1c). In the first case (Figure 1a) shows the dependence of pH value and lead concentration. Phosphate removal efficiency increases with increasing lead concentration even at the highest pH values. According to the solubility diagram, lead is in the form of Pb²⁺ pH> 10, and phosphate in the form of PO₄³⁻

pH>12 and react with each other, forming Pb₃(PO₄)₂ according to reaction (1) (*Fonseca-Montes de Oca et al., 2019*):



Because of its large surface area, there are a large number of active sites for binding of phosphate, and thus leads to their rapid and easy adsorption even at high phosphate concentrations and low doses of nZVI (Figure 1b). The surface of nZVI forms a layer of oxyhydroxide (FeOOH) due to the reaction of iron with water, part of Fe²⁺ or Fe³⁺ is still released with nZVI and forms Fe(OH)₂ or Fe(OH)₃ which is positive in the process of phosphate removal (*Wen et al., 2014*). At a high dose of nZVI, the sorption capacity decreases, the total adsorbent surface area decreases, due to particle aggregation.

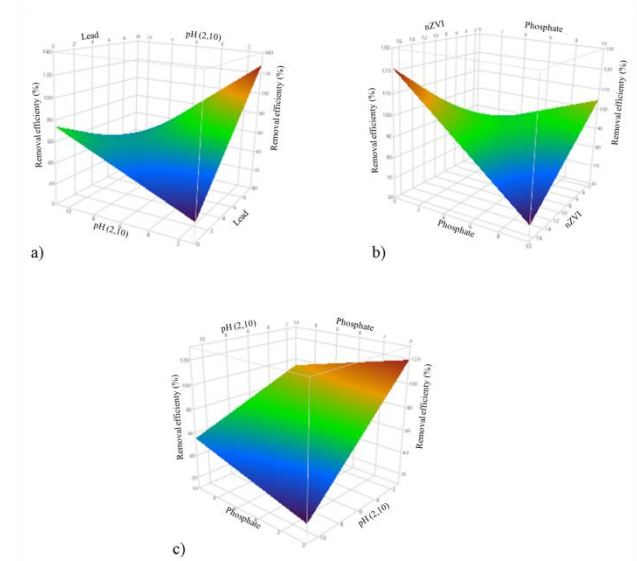
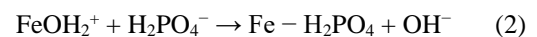


Figure 1. 3D response surface plots for the phosphate removal with the interaction effects between: a) lead concentration and pH; b) phosphate concentration and nZVI; c) phosphate and pH

The dependence of pH value and phosphate concentration is shown in Figure 1(c). By keeping the phosphate concentration at a low level and changing the pH from the basic to the acidic environment, the efficiency of phosphate removal increases.

The optimization diagram (Figure 2) illustrates the efficiency of phosphate removal in the presence of lead as a function of four independent variables. Maximum phosphate removal efficiency of 97.79% proposed under the following conditions: nZVI dose 9 mL, lead concentration 8.76 mgL⁻¹, phosphate concentration 2 mgL⁻¹ and pH value 3. Electrostatic attraction between phosphates in monoanionic H₂PO₄⁻ form and adsorbent surface in an acidic environment increases the removal efficiency of phosphate (reaction 2):



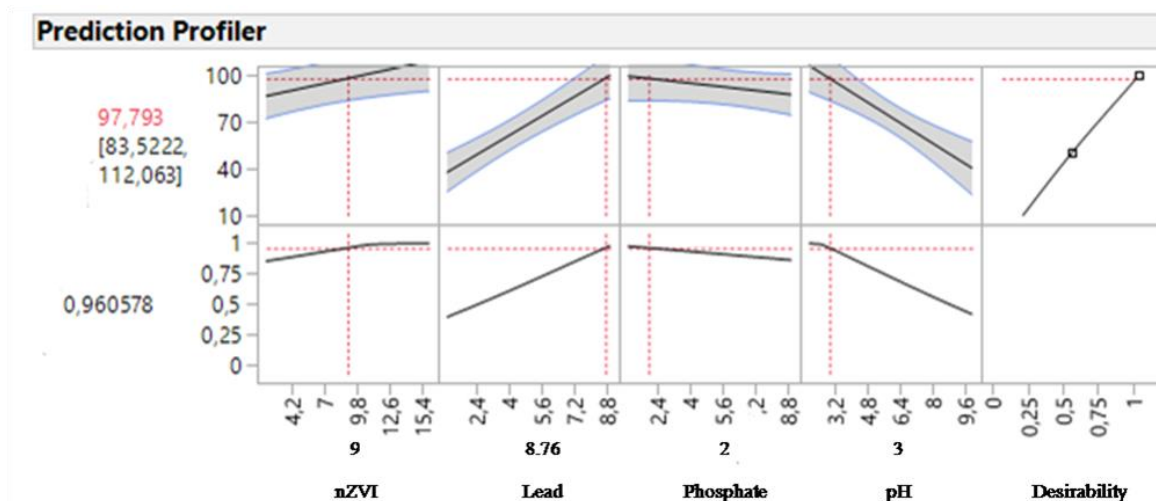


Figure 2. Phosphate removal optimization diagram in the presence of lead

Verification of optimized processes was performed to perform a set of eight - point experiments. Based on this, the confidence interval was calculated with 95% confidence. The proposed efficiencies in the phosphate removal process using nZVI, fit into the confidence interval proposed by the process optimization, which confirms that the models have passed the validation test for this phase of research.

4. Conclusion

Based on the obtained results, it can be concluded that nZVI synthesized with oak leaves is suitable for phosphate removal in the presence of lead from the synthetic aqueous matrix. The applied DSD model contributed to the reduced number of performed experiments with high precision. By optimizing the process, a high removal efficiency of 97.79% was proposed. Process optimization was followed by model verification with a 95% confidence interval. The proposed efficiencies fit into the interval, which means that in this way it was confirmed that the adopted regression model well describes the process of phosphate and lead removal.

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