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Phosphorus Removal by using Nano-scale Iron Materials

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Abstract: Nano-scale Zero Valent Iron (NZVI) was used to remove phosphorus from aqueous solution, and the influence of oxygen and pH were investigated. The higher removal efficiency was obtained from oxic condition. It is because that generated Fe^{2+} and Fe^{3+} will be formed oxide layer on the surface of NZVI which become good adsorbate. And the removal of phosphorus obviously increased when the solution pH was decreased to the acidic side due to the isoelectric point of NZVI. The higher removal efficiency was obtained under oxic and acidic pH condition. According to these results, NZVI was a optimum and useful material for removing phosphorus.

Keywords: Phosphorus removal, Nano-scale Zero Valent Iron (NZVI), water treatment

1. Introduction

Phosphorus is well known as one of the nutrients and finite resources which were non-renewable and non-interchangeable for animals, microbes, plants and algae [1]. Excessive amount of phosphorus in water system cause eutrophication. After eutrophication phenomenon occurred, the fish death will be happened due to the depletion of oxygen concentration in the water. Xu et al. reported that eutrophication threshold of total phosphorus (T-P) for freshwaters was from 0.02 to 0.10 mg/L [2]. Phosphorus was discharged by mainly municipal wastewater, industrial wastewater and agricultural wastewater. Therefore, the excessive amount of phosphorus must be removed before discharged to the nature. In these days, chemical precipitation and enhanced bacteria activity were commonly used to remove the phosphorus, but both of them has demerit [3].

In recent years, research on nanotechnology in the field of water treatment has advanced. Especially Nano-scale Zero Valent Iron (NZVI) is one of the attractive materials for water remediation. It is because NZVI have some advantage such as specific surface area, low cost and non-toxicology. NZVI has been investigated and used in the removal not only phosphorus but also several environmental pollutants such as heavy metals [4], nitrate [5], azo dye [6] from aqueous systems. In this experiment, phosphorus removal by NZVI was investigated by several batch experiments.

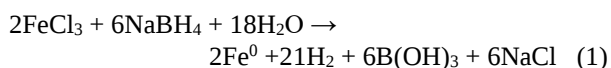
2. Materials and Methods

2.1 Chemicals

The following chemical reagents and materials were used: Sodium borohydride (NaBH_4 , 98.0%, Aldrich Inc., USA), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99.0%, Junsei Chemical Co., Japan) and potassium dihydrogen phosphate (KH_2PO_4 99.5%, Wako Chemical Co., Japan). Nitrogen gas was purged all prepared solutions for de-oxygenation. All chemicals were applied as delivered without further purification.

2.2 Synthesis of NZVI

NZVI was synthesized following this chemical reaction (Eq. (1)) [7]



Precursor 1 was prepared by dissolving 2.1 g of NaBH_4 in 120 mL of deoxygenated deionized water (DIW). Precursor 2 was prepared by dissolving 5.0 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 120 mL of DIW in separate flask. Then precursor 1 was added to precursor 2 using a peristaltic pump at a rate of 16 mL/min. with vigorous stirring at 250 rpm under nitrogen condition at constant temperature $25 \pm 0.5^\circ\text{C}$ using water bath. The synthesis was conducted in 5 L four-neck glass flask and left 20 min. for aging to complete the reaction. The synthesized particle have been filtered by vacuum filter, washed with DIW three times and immediately used in batch experiments.

2.3 Batch Experiments

The several batch experiments were conducted to check adsorption behavior of phosphorus under different conditions. 250 mg of NZVI were added to 300 mL conical flasks filled with 250 mL of phosphorus precursor (50 mg P/L as primary concentration). The flask were tightly closed and stirred by magnetic stirrer (REMIX RSH-6DW, AS ONE Co., Japan) at 200 rpm and 25°C . Anaerobic condition was acquired by deoxygenating the solutions with flowing nitrogen for 15 min. before starting experiments. 5 mL of samples were taken at certain time to analyze phosphorus concentration. To investigate the effect of pH on adsorption of phosphorus by NZVI, anaerobic batch experiments were conducted on the removal of phosphorus of 250 mL solution (50 mg P/L) at three different pH mediums (acidic pH 2, neutral pH 7 and alkaline pH 12).

2.4 Analysis

Phosphorus concentration in solution samples were measured by using an UV-Vis spectrophotometer (DR 3900, Hach Co., USA) via USEPA PhosVer 3 (Ascorbic acid method) at 880 nm.

3. Results and Discussion

3.1 Effect of Oxygen

The Fig. 1 shows the effect of oxygen for removing phosphorus. Phosphorus concentration (oxic) were decreased until 25.18 mg P/L and reached equilibrium after 50 min. Anoxic case, phosphorus concentration were decreased until 26.33 mg P/L and reached equilibrium after 120 min. From these results, oxic condition seems to be effectiveness for removing phosphorus. Under oxygen rich condition, Fe^{2+} and Fe^{3+} generation were enhanced due to the NZVI oxidation. Generated Fe^{2+} and Fe^{3+} will be formed more oxide layer on the surface of NZVI which are good sorbents for contaminants [2].

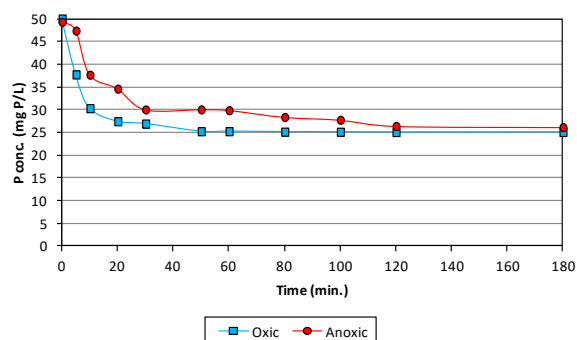


Fig. 1 Phosphorus removal (effect of oxygen)

3.2 Effect of Initial pH

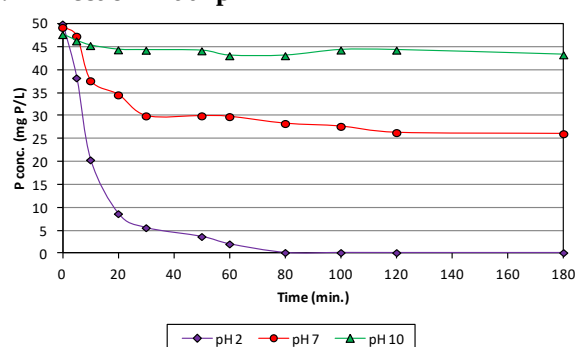


Fig. 2 Phosphorus removal (effect of pH)

The Fig. 2 shows the effect of initial pH on removing phosphorus. Phosphorus concentration (pH 2) were decreased until 0.21 mg P/L and reached equilibrium after 80 min. Also highest phosphorus removal efficiency was achieved up to maximum 99.6%. However the alkaline one, the phosphorus concentration didn't decrease not so much. The highest phosphorus removal efficiency was 9.7%. From these results acidic condition seems to be effectiveness for removing phosphorus. This phenomenon is explained by isoelectric point (IEP) of NZVI. The detail mechanism on phosphorus removal by different pH was shown in Fig. 3.

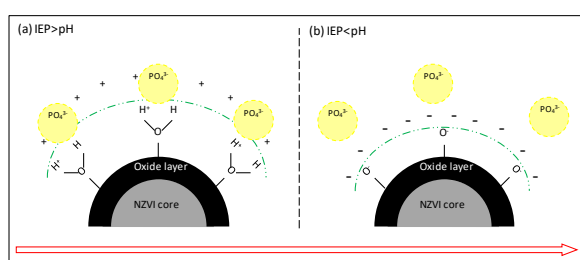


Fig. 3 Removal mechanisms under different pH

IEP of NZVI shows around 8.0; solution pH was lower than IEP, the particle surface became positive charge which makes the surface suitable for anion (PO_4^{3-}) sorption. On the other hand, when the solution pH was higher than IEP, both adsorbent and adsorbate became negative charge, leading to enhanced electric repulsion between them [8]. Moreover the phosphorus anions and OH^- ions will be competed to get the active site thus the adsorption efficiency will be decreased [9].

4. Conclusion

Nano-scale Zero Valent Iron (NZVI) was used to remove phosphorus from aqueous solution, and the influence of oxygen and pH were investigated. The higher removal efficiency was obtained from oxic condition. It is because that generated Fe^{2+} and Fe^{3+} will be formed oxide layer on the surface of NZVI which become good adsorbate. And the removal of phosphorus obviously increased when the solution pH was decreased to the acidic side due to the isoelectric point of NZVI. The higher removal efficiency was obtained under oxic and acidic pH condition. According to these results, NZVI was an optimum and useful material for removing phosphorus.

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