

Nano-Fe₂O₃/bentonite Complexes for Enhanced Phosphorus Removal from Industrial Wastewater

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Abstract. Nano-Fe₂O₃/bentonite complexes were prepared through a reaction between the iron salt solution and the dispersion solution of refined bentonite, and their degradation capability for phosphorus removal was investigated. The results show that Fe₂O₃ nanoparticles anchored between bentonite layers have enhanced capacity for phosphorus removal. Under the conditions of OP₀=10.76 mg/L, IP₀=0.93mg/L and pH=3, nano-Fe₂O₃/bentonite complexes were successfully applied in the treatment of industrial phosphorous wastewater. And the corresponding degradation rate of TP reaches 82% in 0.5hr.

Introduction

Phosphorus discharged from municipal and industrial wastewater treatment plants is a key factor causing eutrophication in surface waters [1]. Meanwhile, its presence also causes many water quality problems including increased purification costs, decreased recreational and conservation value of an impoundments, loss of livestock and the possible lethal effect of algal toxins on drinking water. Therefore, total removal or at least a significant reduction of phosphorus is obligatory in most countries. It is desirable that water treatment facilities remove phosphorus from the wastewater before they are returned to the environment.

Several phosphorus-removal technologies, like metal precipitation [2], constructed wetland systems [3], adsorption by various microorganisms either in a free state or immobilized in polysaccharide gels [4], have been used to remove phosphorus both in large-scale treatment facilities and experimental projects. However, these most common approaches have their limits. For example, bacteria degradation usually requires a long residence time for microorganisms to degrade the pollutant, while chemical precipitation treatment presents considerable difficulties in rendering the precipitates with low concentration.

Since total phosphorus (TP) in industrial wastewater may contain both organic and inorganic contribution, removal of phosphorus from industrial wastewater involves the elimination of both organic phosphorus (OP) and inorganic phosphorus (IP). But it is known that the chemical form of phosphorus greatly affects its removal and recovery in the total phosphorus disposal processes. Moreover, OP has largely been grouped in the “non-reactive” and “non-bioavailable” component. Then it is urgent to find an effective method to degrade simultaneously either OP or IP with high removal ratio.

The objective of this study was to prepare nano-Fe₂O₃/bentonite complexes for enhanced phosphorus removal at low concentration of TP. By intercalating the clay with metal species, nano-Fe₂O₃/bentonite complexes were successfully applied in the treatment of industrial phosphorous wastewater containing both OP and IP.

Experimental Section

Materials. The phosphorous wastewater was obtained from Huayou Cobalt Co., Ltd. (Quzhou, China) with TP₀=11.69 mg/L, in which organic phosphorus and inorganic phosphorus were 10.76mg/L and

0.93mg/L, respectively. Chemical grade $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, FeCl_3 , H_2O_2 and H_2SO_4 were supplied by Sinopharm Chemical Reagent Co., Ltd. without further purification.

Experimental Method

Synthesis of Nano- Fe_2O_3 /bentonite Complexes

Nano- Fe_2O_3 /bentonite complexes were synthesized in the following method. 10g clay was mixed with 1L 0.65M H_2SO_4 and stirred for 0.5hr at room temperature. After supernatant liquid being dumped, water was added into the flask and kept the volume of solution back to 1L. Being washed repeatedly for several times, the obtained sample solution was added into the flask and bubble argon for 0.5h. 3.519g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 2.057g FeCl_3 were added in 15 min and stirred continuously for 9hr under room temperature. Then ammonium hydroxide was added to increase the pH value of the wastewater beyond about 10. Being stirred for additional 2h, the solid was filtered under vacuum condition and dried for 24h in oven. Upon cooling, the solid was broken to powders for the following use.

Adsorption Kinetics

The experiments were conducted using an initial TP concentration of 11.69 mg/L, 2.15 g/L of Nano- Fe_2O_3 /bentonite complexes, shaking rate (250 rpm) under pH 3.0 and 30°C. After the adsorption time arrived, samples were removed and the content of TP was measured.

Effect of pH

In the adsorption process for investigating the effect of pH on phosphorous degradation, 0.215g nano- Fe_2O_3 /bentonite complexes were added into 100 ml phosphorous wastewater. Under constant pH conditions at pH values from 3.0 to 9.0, all samples were shaken at 30°C for 2hr. Then the suspensions were filtered and the content of TP was determined by spectrophotometric method. The difference of TP before and after shaking was used to calculate the adsorption capacity of nano- Fe_2O_3 /bentonite complexes.

Effect of Nano- Fe_2O_3 /bentonite Complexes Amount

Various amounts (0.043g, 0.129g, 0.215g, 0.323g) of nano- Fe_2O_3 /bentonite complexes and 100 ml phosphorous wastewater were added into the Erlenmeyer flask, respectively. Being kept at 30°C under stirring for 2 h, the adsorption solution was filtered. And the content of TP in supernatant liquid was determined by spectrophotometric method. Then, difference of TP before and after shaking was used to calculate phosphorus removal ratio.

Results and Discussion

Adsorption Kinetics

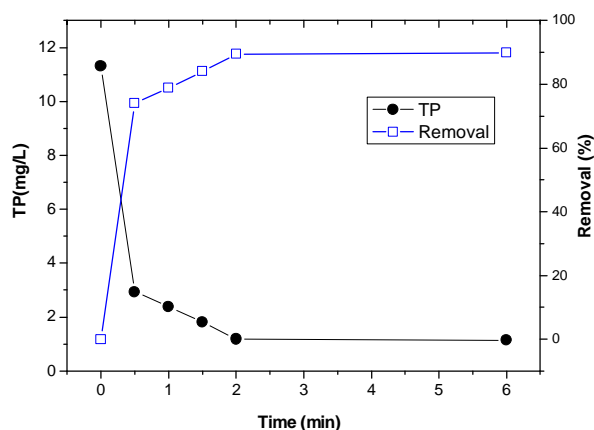


Fig. 1 Adsorption kinetics curve of nano- Fe_2O_3 /bentonite complexes.
($\text{OP}_0=10.76\text{mg/L}$, $\text{IP}_0=0.93\text{mg/L}$, and $\text{pH}=3$)

Adsorption kinetics was investigated to evaluate both the rate of phosphorous adsorption and the equilibrium time required for the adsorption. From the adsorption kinetics curves displayed in Fig. 1, it

could be found that nano-Fe₂O₃/bentonite complexes show excellent phosphorous disposal ability. The fact that removal rate increased quickly in 2min indicates that mass-transfer phenomena were not a limiting step when nano-Fe₂O₃/bentonite complexes were used as adsorption agents.

Effect of pH

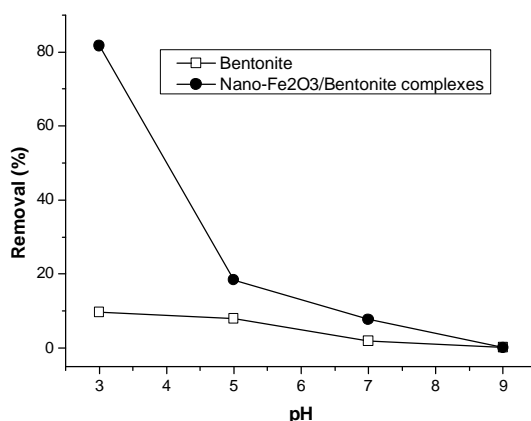


Fig. 2 Influence of pH on removal ratio in phosphorous wastewater. (OP₀=10.76mg/L, IP₀=0.93mg/L)

Since pH of the solution is one of the most important factors which influence the adsorption behavior of any adsorbent material, Fig. 2 demonstrates the effect of pH on the disposal of phosphorous wastewater by different adsorbents. It can be seen that the removal rate of nano-Fe₂O₃/bentonite is higher than that of raw bentonite. Especially, at strong acidic pH values (3.0-5.0), enhanced phosphorus removal is observed and the maximum removal rate of 82% is obtained at pH3.0. Increasing the pH values from 5 to alkaline conditions (pH 9), the removal of phosphorus increased slowly. Being compared with the results taken from raw bentonite, whose maximum removal rate of is about 9.7%, it is reasonable to consider that the presence of nano-Fe₂O₃/bentonite complexes greatly improved phosphorus removal in wastewater treatment.

Effect of Nano-Fe₂O₃/bentonite Complexes Amount

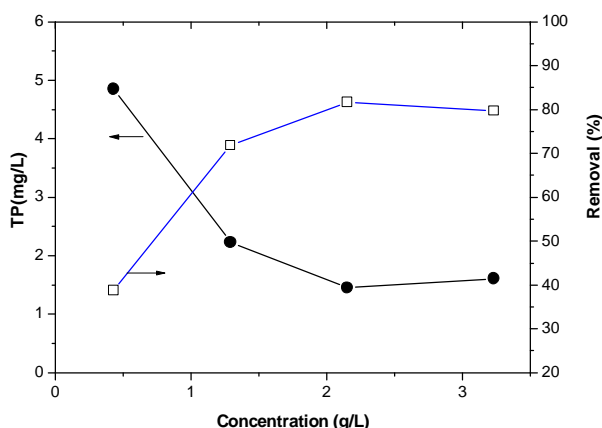


Fig. 3 Relationship between the degradation effect and dosage for nano-Fe₂O₃/bentonite complexes

Relationship between the degradation effect and various dosages of nano-Fe₂O₃/bentonite complexes was given in Fig. 3. It can be seen that when the content of modified bentonite increased from 0.4 to 3.2 (g/L), the removal rate of phosphorus increased rapidly from 39% to 82%. In view of the weak contribution of raw bentonite, nano-Fe₂O₃ should play a dominating role in modified bentonite for

phosphorous removal. Therefore, by increasing the content of modified agents in disposal process, better phosphorus removal performance can be expected.

Conclusions

Nano-Fe₂O₃/bentonite complexes can combine the typical characters of nano-particles and multilayer structure in the disposal of phosphorous wastewater. Then, enhanced TP degradation efficiencies were obtained in the treatment of phosphorous wastewater. Although lots of degradation work has been independently done for organic phosphorus or inorganic phosphorus, simultaneous removal of both organic and inorganic phosphorus with high efficiency still needs lots of efforts in future research works.

Acknowledgements

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References

- [1] D. Cordell, A. Rosemarin, J.J. Schröder and A.L. Smit: Chemosphere Vol.84 (2011), p. 747
- [2] H.M. Huang, J.H. Liu and Y. Jiang: Scientific Reports 5, Article number: 16601 (2015)
- [3] X.O. Wang, Y.M. Tian, X.H. Zhao, S. Peng, O. Wu and L.J. Yan: Bioresource Technology Vol.198 (2015), p.7
- [4] H.Y. Lu, L.Z. Yang, S. Shabbir and Y.H. Wu: Environmental Science and Pollution Research Vol. 21(2014), p. 8782