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Adsorptive removal of phosphate from wastewater with magnetite particles: a study on the particle size optimization

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Abstract

Mill scale - derived magnetite particles were synthesized and utilized in this study as an adsorbent for phosphate removal. Results obtained in this study showed that alkaline media concentration and alkaline species have a significant effect on the size distribution and phosphate adsorption capacity of synthesized magnetite particles. It was observed that increasing the alkali concentration of both bases results in a decrease in the size and size distribution of the particles. The size range of synthesized magnetite particles was 0.3-1.8 μm and 0.4-3.2 μm in diameter when NaOH and NH₄OH was used for co-precipitation, respectively. When the dosage rate of alkaline solution was decreased from over 100 to 10ml/min, much higher size particles (45-300 μm in diameter) can be obtained. Sufficient agglomeration of sub-micron size magnetite crystals seemed to be caused by decreased alkali dosage rate and it was responsible for the increase in overall particle size distribution. Moreover, it was found that mill scale - derived magnetite is an effective adsorbent for the removal of phosphate from wastewater. Magnetite particles synthesized with NaOH solution showed the phosphate adsorption capacity over 10mgP/g. series.

1 Introduction

Recently, the utilization of industrial wastes or by - products for phosphorus removal has been given a great attention. In this study, mill scale-derived magnetite particles were applied for adsorptive removal of phosphate from water/wastewater as a cost-effective material. Mill scale is an

iron waste produced from the hot-rolling process of steel factories. Its specific production is approximately 35-40kg/ton of hot-rolled iron product (International Iron and Steel Institute, 1987). Typical mill scale is composed of 59.7% (w/w) wustite (FeO), 8.3% maghemite ($\gamma - \text{Fe}_2\text{O}_3$), 23.5% magnetite (Fe_3O_4), and 8.5% the others (Doliente et al., 2017). It is known that phosphate ion has a strong affinity toward metal oxides. This idea is widely exploited that the mechanism of phosphate removal from aqueous solution by adsorptive separation has been described by many researchers. The ability of magnetite particles to adsorb phosphate has been studied thoroughly. Among the various techniques for the production of magnetite, co-precipitation method is the commonly used technique. Choi et al. (2016) and Chun et al. (2015) proved that magnetite particles can be produced from mill scale. The success of the synthesis is due to the fact that mill scale contains significant amounts of iron oxides that can be used in phosphorus removal.

The objectives of this study were (i) to synthesize and characterize magnetite from mill scale, (ii) to examine parameters affecting the particle size and size distribution of magnetite particles including alkaline species, and concentration of bases used, and (iv) to assess the ability of mill scale - derived magnetite to remove phosphate from wastewater.

2 Methodology

2.1 Mill scale pretreatment

The raw mill scale was obtained from P steel company, Korea. Mill scale showed plate-type shape with a diameter of $<20\text{mm}$. In order to remove grease and oil, mill scale was washed with 0.1N NaOH solution followed by 3-times tap water cleaning. After drying, the samples were pulverized with a mechanical grinder (pin-mill system, model HKP-100, Korea Pulverizing Machinery, Gyeonggi, Korea) to homogenize and minimize the particle size of the sample. The samples were then sieved using standard meshes into five size fractions: $>300\ \mu\text{m}$, $150\text{-}300\ \mu\text{m}$, $75\text{-}150\ \mu\text{m}$, $45\text{-}75\ \mu\text{m}$, $<45\ \mu\text{m}$. Just $45\text{-}75\ \mu\text{m}$ particles were used for the following process of magnetite synthesis because the amount of this size range particles was the highest.

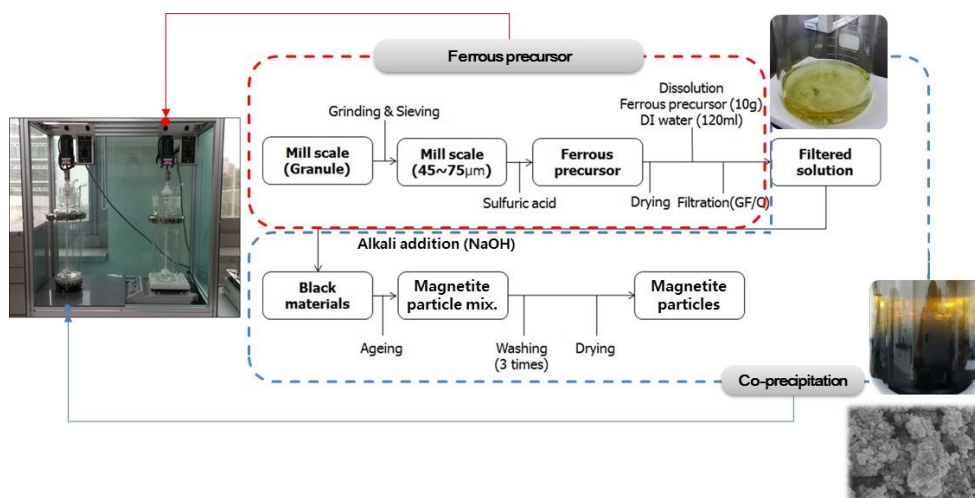


Figure 1: The process for synthesis of magnetite particles

2.2 Magnetite synthesis and characterization

Co-precipitation method was the procedure used to synthesize magnetite using mill scale (Figure 1). The ferrous precursor was obtained by mixing mill scale and concentrated sulfuric acid for 24 h under an inert atmosphere at 60°C. The precursor was then dissolved in deionized water and filtered. Into the filtrate, a base was added. The effect of the alkali species was determined by using two kinds of base: NaOH (strong base) and NH₄OH (weak base). Moreover, the concentrations of the bases were adjusted to analyze its effect. The synthesized magnetite particles were characterized using X-ray powder diffraction (XRD) and the particle distribution was also analyzed. The particle size distribution of the synthesized magnetite was analyzed with a SediGraph 5100 particle size analyzer (Micromeritics Japan, Chiba, Japan).

2.3 Batch adsorption experiments

Batch adsorption isotherm tests with the synthesized adsorbents at 298 and 308 K were done in a mechanical shaker (J - USRC, Jisico). The adsorption was done at pH 6 and the mixture was mixed for 24 h at room temperature. The synthesized magnetite particles (1 g/L) were dispersed in the phosphate solution of which initial concentrations were 10, 20, 30, 40, 50, and 60 mgP/L. Samples were collected and filtered prior to phosphate anion determination. The phosphate concentration was analyzed using a Thermo Scientific™ Dionex™ ICS - 1000. The wastewater samples were collected from G wastewater Plant located in South Korea. The samples were filtered first using Whatman paper filter (110 mm diameter).

3 Results and discussion

3.1 Physical and chemical properties of the synthesized magnetite particles

The XRD analysis results of raw mill scale and acid/base treated mill scale are shown in Figure 2(a). From the analysis of XRD patterns, major components of mill scale are wustite (FeO), maghemite (Fe₂O₃), and magnetite (Fe₃O₄). No significant change in mill scale composition was found just after base treatment (MSB, 0.1N NaOH solution). However after acid treatment (MSA, 0.7N HCl solution), wustite content might be significantly decreased as shown in Figure 2(b). With sequential treatment of acid and base (MSAB), we could increase magnetite content remarkably and the synthesized particles showed almost same peak pattern introduced in JCPDS (Joint Committee on Powder Diffraction Standard) reference of magnetite (Figure 2(b)). Typical method for synthesis of high purity magnetite particles is to use ferric and ferrous chloride with an appropriate mixing ratio (Eom et al., 2010). But in our study, over 95% purity magnetite particles could be obtained with much cheaper raw materials.

3.2 Effects of alkali species on the properties of synthesized magnetite particles

The XRD patterns of the synthesized particles prepared from water - soluble mill scale - derived precursor at various concentrations of (0.5, 0.67, 1, 2 N) NaOH and (0.6, 0.8, 1.2, 2.4 N) NH₄OH were analyzed and the results are shown in Figure 3. Samples prepared using NaOH concentration of 0.5, 0.67, and 1 N and samples prepared using NH₄OH concentration of 0.6, 0.8, and 1.2 N confirms

the formation of magnetite phase of iron oxide with inverse spinel structure (JCPDS file no. 19 - 0629). The observed magnetite peaks were (220), (311), (400), (422), (511), and (440). Moreover, a goethite peak of (110) was found in the XRD pattern of the samples prepared with 2 N NaOH and 2.4 N NH_4OH .

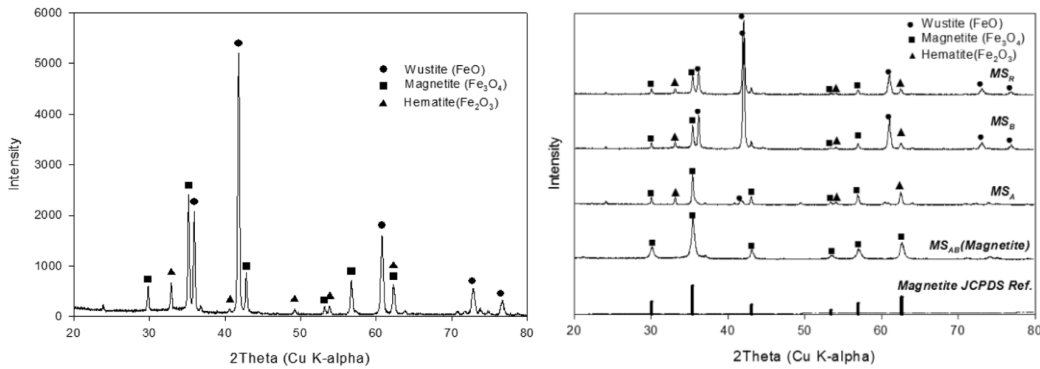


Figure 2: XRD pattern of raw mill scale (a) and acid/base treated mill scale (b)

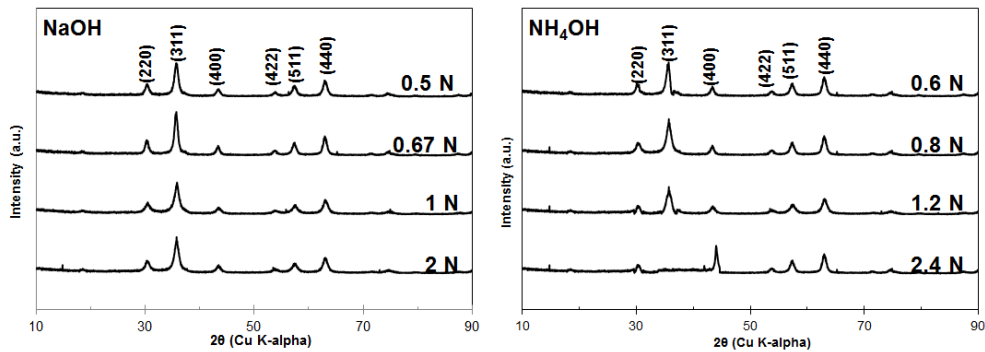


Figure 3: XRD pattern of the synthesized magnetite particles with different alkali solutions

The PSD (particle size distribution) analysis for the synthesized magnetite particles is presented in Figure 4. The particle size of samples prepared using NaOH was relatively smaller than the samples prepared using NH_4OH . In both cases, the size distribution broadness of the magnetite particles is decreased by increasing the concentration of the bases. Daou et al (2007) also emphasized the importance of alkali concentration on magnetite particle size distribution.

3.3 Phosphate adsorption characteristics

Adsorption kinetics of phosphate was well described by a pseudo - second - order kinetic model which assumes that the adsorption occurs on localized sites with no interaction between phosphate anions, and maximum adsorption represents saturated monolayer adsorption. Furthermore, the two - parameter Langmuir model (Eq. (1)) provides a better fit to experimental data compared to Freundlich isotherm model (Eq. (2)) indicated by the higher value of correlation coefficient (R²) (Figure 5).

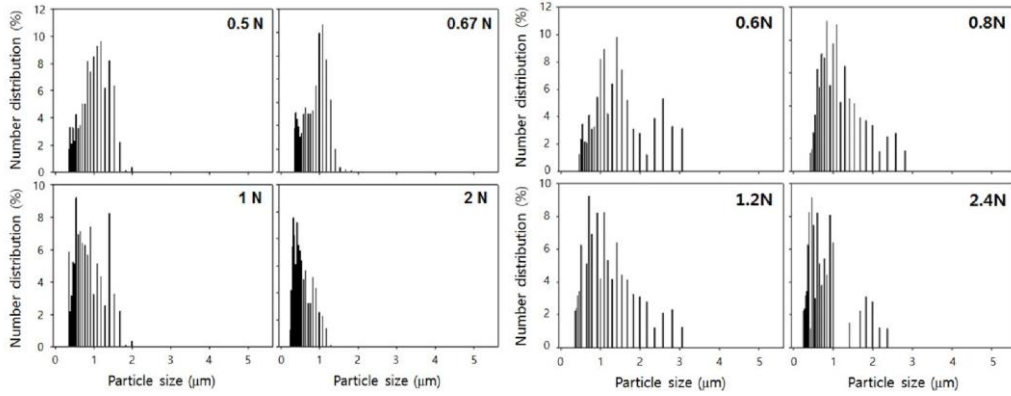


Figure 4: The size distribution of the magnetite particles produced from co-precipitation with NaOH (left) and NH₄OH (right)

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

$$q_e = K_F C_e^{1/n} \quad (2)$$

Where, q_e = equilibrium adsorption capacity (mg/g)
 C_e = equilibrium concentration of solution (mgP/L)
 q_m = maximum adsorption capacity (mg/g)
 K_L = Langmuir affinity constant
 K_F = Freundlich adsorption capacity constant
 $1/n$ = Freundlich adsorption intensity constant

The equilibrium isotherm model analyses are shown in Fig. 5. The application of the Langmuir isotherm model is based on monolayer coverage of adsorbent surfaces by the adsorbate. The adsorption process takes place at specific homogeneous sites of equal energy in which no interaction occurs between adsorbed species. The Freundlich isotherm model is based on the multilayer adsorption of an adsorbate onto heterogeneous surfaces. The estimated parameters from each isotherm model are summarized in Table 1. Indicated by the higher value of correlation coefficient (R^2), the Langmuir isotherm model provides a better fit to the experimental data compared with the Freundlich isotherm model. From the Langmuir model, the maximum phosphate adsorption capacity (q_m) was determined to be 4.9529 and 8.7873 mg/g at an adsorption temperature of 298 and 308 K, respectively.

It was found that the particles' P adsorption capacity was strongly affected by the alkaline media concentration and alkaline species (see Figure 6). Samples prepared using NaOH have a higher adsorption capacity than the samples prepared using NH₄OH. This is due to the smaller particle size distribution of NaOH - based particles. Additionally, the higher pH and alkaline concentration change the chemical composition of the crystals that leads to a decrease in the interfacial tension and free enthalpy of particles allowing the increase of surface to volume ratio.

The result in the batch adsorption experiment that utilized wastewater samples as phosphorus - contained water body indicated that phosphate removal efficiency of the mill scale - derived magnetite first increased and slowly decreased as the time of contact increases. The phosphate

concentration in the filtered wastewater was found to be ~10 ppm. The highest P removal efficiency was 42.72%.

Table 1: Estimated value of the isotherm parameters for phosphate adsorption on magnetite

Isotherm model	Kinetic parameter	Temperature (K)	
		298	308
Langmuir	K_L (L/mg)	0.1409	0.1093
	q_m (mg/g)	4.9529	8.7873
	R^2	0.9481	0.9974
Freundlich	K_F (L/g)	1.4706	2.0162
	n	3.4905	2.8952
	q_m (mg/g)	4.7528	8.2928
	R^2	0.9466	0.9602

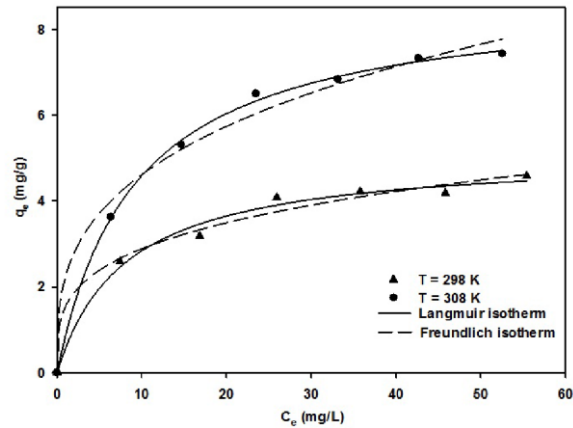


Figure 5: Isotherm plot for phosphate adsorption on magnetite particle

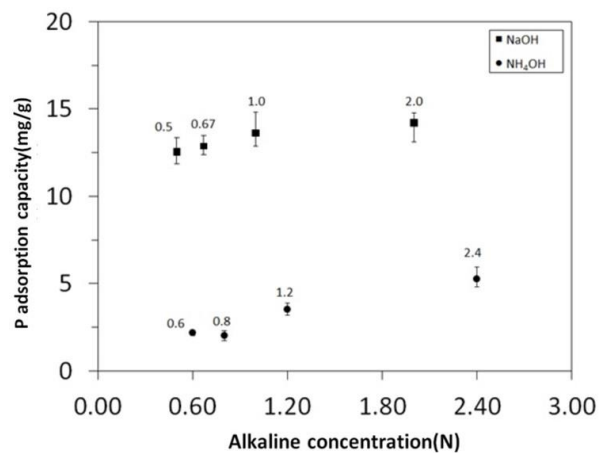


Figure 6: Adsorption capacity of the magnetite particles synthesized using various alkaline concentrations (NaOH: 0.5 - 2.0 N, NH_4OH : 0.6 - 2.4 N)

4 Conclusion

A cost effective adsorbent for phosphate removal from wastewater was successfully synthesized from the waste mill scale. The major synthesis process is consisted of ferrous precursor production and co-precipitation. From this process high purity magnetite particle with various particle size could be obtained. Alkali species and concentration used for co-precipitation affect the size distribution of the magnetite particles. Lower particle size might be responsible for active crystallization and inactive agglomeration. The synthesized magnetite particle showed a good phosphate adsorption efficiency and Langmuir isotherm model described the phosphate adsorption behaviour better than Freundlich model. The maximum phosphate adsorption capacity was about 8.8mgP/g.

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References

- Choi, Y.G., Phearom S., Jonica E.D., Maeng, M.S. and Choi, E.S. (2016) Adsorptive removal of arsenate using inorganic magnetite particles, *Desal. Wat. Treat.* 3994 (June). DOI:10.1080/19443994.2016.1164085
- Chun, H.C., Choi. Y.G. (2015) A Study on the mill-scale pretreatment and Magnetite Production for Phosphate adsorption, *J. Korean Society of Environ. Eng.*, 37(4), pp. 246-252
- Daou, T.J., Begin-Colin, S., Greneche, J.M., Thomas F., Derory, A., Bernhardt, P., Legare, P., Pourroy, G. (2007). Phosphate adsorption properties of magnetite-based nanoparticles. *Chemistry of Materials*, 19, pp. 4494-4505
- Doliente, J.E., Kim, Y.J., Nam, H.W. and Choi, Y.G. (2017) Mill Scale-Derived Magnetite Particles: Effective Adsorbent for the Removal of Phosphate in Aqueous Solutions, *J. Environ. Eng.*, 143(12), 04017076, DOI:10.1061/(ASCE)EE.1943-7870.0001278
- Eom, T.H., Tuan, H.T., Kim, S.J. and Suhr, D.S. (2010) Synthesis of Iron Oxide Using Ferrous and Ferric Sulfate, *Korean J. Mater. Res.*, 20(6), 301-306
- International Iron and Steel Institute. (1987) *The management of steel industry by-products and waste*, Brussels Committee on Environmental Affairs, Brussels, Belgium