Removal and recycle of phosphate from treated water of sewage plants with zirconium ferrite adsorbent by high gradient magnetic separation

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Abstract. Zirconium ferrite particles are good adsorbent for phosphate ions. Magnetic separation characteristics for removal of phosphate from treated water of sewage plants with the adsorbent have been studied to prevent eutrophication of semi-enclosed bay, e.g. the bay of Tokyo. Based on the adsorption for the phosphate ions and ferromagnetic properties of the zirconium ferrite adsorbent, high gradient magnetic separation characteristics with using superconducting magnet was discussed. Very rapid magnetic filtration velocity, i.e. 1m/s, and regeneration properties of the adsorbent indicate that the zirconium ferrite is the excellent adsorbent for phosphorus removal and recycle from treated water of large scale sewage plants.

1. Introduction
In the case of the bay of Tokyo, 5-6 tons of phosphate flow into the bay in the treated discharge water from the sewage disposal plants per day in spite of reducing phosphate to below the quality standard, i.e. 1 mg/L, by the advanced wastewater treatment methods A2O. Fishes and shells so called “Edomae” are decreasing due to the red tide and the blue tide generated by eutrophication by nutrient inputs, i.e. phosphorus and nitrogen. Discharge water from sewage treatment plants is a major source of nutrient inputs into aquatic systems. Scientists of oceanography have proposed to further decreasing of phosphate to 60% of 1 mg/L to prevent the eutrophication. To meet their demands, we studied applicability of the high gradient magnetic separation HGMS technology with zirconium ferrite adsorbent to remove the phosphate from the discharge water to less than 0.1 mg/L level. The HGMS with superconducting magnet not only has great potentiality to reduce the phosphate from the discharge water rapidly without generation of secondary products or sludge etc, i.e. zero-emission process, but possibility to reuse of trapped adsorbent.

Zirconium ferrite particles are good adsorbent for phosphate ions. National Institute for Environmental Studies NIES demonstrated the ability of the zirconium ferrite as the adsorbent of the phosphate in the Kasumigaura project and developed a phosphate recover station. Recycle of the phosphate is possible by washing zirconium ferrite particles with NaOH solution. The phosphate is, therefore, able to recycle, by the same method in the case of HGMS. USA prohibit export of phosphorous ore in 1997 and China is also going to stop export. Japan has no phosphorous resources, therefore, recycle of the phosphate in the discharge water from the sewage disposal plants is a very important challenge for us.
2. Experimental
Zirconium ferrite ZrFe$_2$(OH)$_6$ adsorbent was offered by Japan EnviroChemicals Ltd. The adsorbent has sphere structure with 0.7 mm diameter for the filtration method, i.e. developed for the Kasumigaura project. The adsorbent particles contain not only zirconium ferrite particles with around 10 micron diameter but also binder to form the spherical shape.

SQUID magnetization measurement system MPMS-3 was used for magnetization measurements. Experimental apparatus for the HGMS with a 10 T superconducting magnet having 10 cm room temperature bore diameter is shown in Fig.1. At the bore center, filter matrix of ferromagnetic stainless wire with 100 micron diameter was located.

Adsorption time dependence of the removal ratio for the phosphate in sample water to the adsorbent was measured.

Phosphate density in sample water was measured with a spectro photometer.

Typical magnetic separation experiment was conducted for discharge water offered from a sewage treatment plant under the condition with using 800 ppm zirconium ferrite adsorbent, 15 minutes adsorption time, at 10 T and at 0.03 L/sec flow rate. The phosphate density in the discharge water was 0.86 mg/L.

3. Results and discussion
Zirconium ferrite adsorbent has ferromagnetic characteristics as shown in Fig.2. owing to Fe ions in the ferrite structure. Upper limit of the treatment water velocity for the HGMS, i.e. a magnetic velocity $v_m$, is given by

$$v_m = \frac{2}{9} \left( \frac{\mu_0 \chi M_s H_0 R^2}{\eta a} \right)$$

where $M_s$ is the saturation magnetization of the filter matrix, $\chi$ is the magnetic susceptibility of the adsorbent, $\eta$ is the water viscosity, $R$ is the adsorbent particle radius, $a$ is matrix wire radius, $H_0$ is applied magnetic field[1]. In the case of ferromagnetic adsorbent, the saturation magnetization of the adsorbent $M_s$ can be used instead of the $\chi H_0$. Rapid theoretical velocity of $v_m = 1$ m/s is obtained by substitution $M_s$ for $\chi H_0$.

Adsorption characteristic of the phosphate to the zirconium ferrite adsorbent is shown in Fig.3. The results indicate that more than 90% of phosphate in the discharge water can be removed in 5 minutes.

The HGMS could reduce the phosphate density in the discharge water offered by a sewage treatment plant from 0.86 mg/L to 0.006 mg/L under the typical condition. The removal ratio for the
phosphate by the zirconium ferrite adsorbent is 99%. This result shows that the HGMS technology with the zirconium ferrite adsorbent is useful for preventing the eutrophication of semi-enclosed bay by it’s introduction into sewage treatment plants. The technology can eliminate the advanced wastewater treatment A2O process in a sewage treatment plant for reduction of phosphate.

Captured adsorbent to the filter matrix is easily detrapped from the matrix by decreasing magnetic field of a suprconducting magnet. Phosphate ions adsorbed by zirconium ferrite particles can be removed with NaOH solution and the zirconium ferrite adsorbent is able to use repeatedly. Zero-emission process, therefore, can be achieved.

The principle of the NIES phosphate recover station developed for the Kasumigaura project is available for the recycle system of the phosphate.

4. Conclusion
Ferromagnetic properties revealed in this study show that the zirconium ferrite is excellent adsorbent of phosphate for HGMS.

High separation velocity of HGMS with superconducting magnet estimated from the magnetic velocity is suitable to remove phosphate from discharge water of large sewage treatment plants.

Zirconium ferrite is reusable adsorbent, therefore, phosphate removal in zero-emission is possible. Phosphorus recycle is possible with using the principle of the NIES recover station.

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References
[1] Watson J H P et al. 1996 Minerals Engineering 9 973.