Flocculation-Magnetic Separation Technology for the Rapid Treatment of First Flush Rain

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Abstract. In order to rapid treatment of first flush rainwater, a new flocculation-magnetic microsphere was prepared. And magnetic microspheres were prepared using the modified Stöber method. Magnetite (Fe₃O₄)-silica (SiO₂) core-shell microspheres have superparamagnetism verified by using XRD, FTIR and VSM analysis. Also, Fe₃O₄/SiO₂ (FS) microspheres have no significant reduction after at least reused five times. The optimal feeding order and conditions were flocculant, magnetic powder and PAM, reaction temperature 25°C, static sedimentation time 30 min, and pH=7. Under the optimized condition, 62% of COD and 98% of turbidity were removed. Especially, Fe₃O₄/SiO₂ microspheres can effectively adsorb heavy metal ion.

1. Introduction
The first flush rain is a surface pollution source with dispersion of spatial and temporal and heterogeneity [1]. These characteristics determine that the control of first flush rainwater will be very complicated [2]. How to fully collect and properly use rainwater with attributes of resources and pollution has become a promising and meaningful topic.

For flocculation-magnetic separation technology [3], flocculation combines with magnetic separation to enhance flocculation effect, shorten settling time, reduce sludge volume and water content, greatly improve sewage treatment efficiency, shorten water treatment time, reduce structure volume and reduce cost. It has made great progress on the field of environmental protection [4,5]. Therefore, it is extremely suitable for pre-treatment of first flush rainwater.

In this present work, by using a modified Stöber method, new magnetite (Fe₃O₄)-silica (SiO₂) core-shell microspheres were prepared. Also, COD, turbidity and heavy metal ion were removed at the rapid treatment of first flush rain.
2. Experimental

2.1. Synthesis of Fe$_3$O$_4$/SiO$_2$ microspheres
In this work, Fe$_3$O$_4$/SiO$_2$ microspheres were prepared by a normally modified Stöber method. And magnetite Fe$_3$O$_4$ microspheres with four different sizes of 200, 300, 400 and 500 mesh were respectively dispersed in a mixed solution. Firstly, 240mg Fe$_3$O$_4$ microspheres scattered in 100mL 2-propanol before 15min vigorously stirred. Also, the solution scattered in the 2-propanol (300mL) and DD-water (100mL). Then, 3.5 mL ammonia solution was added dropwise during 40min vigorously stirred. Next, 240μL TEOS was mixed in the solution during 2.5 hr vigorously stirred at 35$^\circ$C. Then, they were washed and dried overnight at 60$^\circ$C.

2.2. Flocculation design
The dynamic adsorption was studied by adding the order of flocculant, magnetic powder and PAM. The test was carried out as according to the above flocculated process, at pH = 7.0 ± 0.5, magnetic particle size = 200 mesh, 300 mesh, 400 mesh, or 500 mesh. In order to identify the residual turbidity, COD, and heavy metal (Ni, Hg, Pb), supernatant samples were gathered from 2 cm below the liquid surface during reaction time of 30min.

3. Results and Discussions
X-ray diffraction patterns of magnetic microspheres were measured with a D/MAX-2500 X-ray diffractometer (XRD, Rigaku. Japan) as shown Figure 1. Figure 1 suggested that the diffractogram peaks should be the characteristic peaks of the Fe$_3$O$_4$, which might be observed at $2\theta = 24.72^\circ$, 30.16$^\circ$, 35.58$^\circ$, 43.26$^\circ$, 53.68$^\circ$, 57.04$^\circ$, 62.72$^\circ$, and 74.10$^\circ$. And Fe$_3$O$_4$ with cubic spinel structure is of magnetic and segregative.

Figure 1. XRD patterns of various Magnetic seeds(a) Fe$_3$O$_4$, (b) Fe$_3$O$_4$/SiO$_2$

The chemical bonding and composition information of Fe$_3$O$_4$/SiO$_2$ and Fe$_3$O$_4$ microspheres were carried out by Fourier Transform Infrared Spectroscopy (FTIR, MultiGas 2030) were shown in Figure 2. Both Fe$_3$O$_4$/SiO$_2$ and Fe$_3$O$_4$ had the high-intensity absorption peak about at 500cm$^{-1}$, which was contributed by the bending vibration of the Fe$_3$O$_4$. The FTIR characteristic peaks of Fe$_3$O$_4$/SiO$_2$ were detected at 1403-1232cm$^{-1}$(1403-1232cm$^{-1}$ stands for the stretching modes of Si-O-Si). Compared to
Fe$_3$O$_4$, SiO$_2$ is successfully covered the surface of Fe$_3$O$_4$ core. Hence, it can be seen that Fe$_3$O$_4$/SiO$_2$ is a microsphere with core-shell structure.

Figure 2. FT-IR spectra of various Magnetic seeds (a) Fe$_3$O$_4$, (b) Fe$_3$O$_4$/SiO$_2$

Figure 3 showed the magnetic hysteresis curves of Fe$_3$O$_4$ microspheres and Fe$_3$O$_4$/SiO$_2$ microspheres, respectively using a vibrating sample magnetometer (VSM). It's obvious that both Fe$_3$O$_4$ and Fe$_3$O$_4$/SiO$_2$ microspheres exhibited superparamagnetic properties. The saturation magnetization (Ms) of Fe$_3$O$_4$, and Fe$_3$O$_4$/SiO$_2$ were about 39.2 and 26.9 emu/g, respectively. Compared to Fe$_3$O$_4$, the decrease of Ms for Fe$_3$O$_4$/SiO$_2$ microspheres could be attributed to the introduction of non-magnetic SiO$_2$ decoration. Hence, the as-prepared Fe$_3$O$_4$/SiO$_2$ microspheres appeared high magnetic separability, which could make quick magnetic separation and re-dispersal by an external permanence magnet.

Figure 3. Magnetic hysteresis curves of various magnetic seeds at room temperature (a) Fe$_3$O$_4$, (b) Fe$_3$O$_4$/SiO$_2$.

Besides magnetic and flocculation, the stability was importance to Fe$_3$O$_4$/SiO$_2$ microspheres for their practical applications. In order to identify the stability of Fe$_3$O$_4$/SiO$_2$ microspheres, Fe$_3$O$_4$/SiO$_2$ as a representative sample was carried out in the repeatability experiments. Experiments of 5 batches were
implemented in reactors. After reaction stopped, the Fe₃O₄/SiO₂ microspheres were allowed to be separated by the imposed magnetic field. The results of each batch were shown in table 1. Results suggested that no obvious decrease could be obtained, which further demonstrated that Fe₃O₄/SiO₂ microspheres were stable and high effective for flocculation-magnetic separation technology of first flush rain.

Table 1. Experiments of 5 batches for Fe₃O₄/SiO₂ at room temperature

| Reuse | Addition (g) | Recycling (g) | Recovery rate (%) | Turbidity (%) | COD (%) |
|-------|--------------|---------------|-------------------|---------------|---------|
| 1     | 2.00         | 1.98          | 99.0              | 98.3          | 62.3    |
| 2     | 2.00         | 1.99          | 99.5              | 98.2          | 58.4    |
| 3     | 2.00         | 1.97          | 98.5              | 98.5          | 66.2    |
| 4     | 2.00         | 1.98          | 99.0              | 98.6          | 70.1    |
| 5     | 2.00         | 1.97          | 98.5              | 98.4          | 68.2    |

In this work, magnetic powders with the different particle size of 200, 300, 400, 500, 600 mesh were investigated on experiments of magnetic flocculation in Figure 4. Figure 4 showed that the removal rate of first flush rain increased with the decreasing of particle size of Fe₃O₄/SiO₂. For the flocculation-magnetic Separation Technology, the removal rate of turbidity was about 98% after stewing for 30min, and COD, Ni, Hg and Pb were respectively 60%, 40%, 50% and 90%. This may have been due to decreasing the specific surface area of magnetic powders as the particle size increases, what contact area with the contaminant greatly reduced. Moreover, the larger particle magnetic powder was more easy to sink, owing to comparatively large magnetic strength of the magnetic powder. However, the particle size is too small. It is difficult to thoroughly separate from water in practical applications. In combination with practicality and economic considerations, the magnetic powder particles should be 400 mesh.

Figure 4. Effects of particle size on the flocculation-magnetic of first flush rain for the Rapid Treatment (20 mg·L⁻¹ PAC+200mg·L⁻¹ magnetic powder + 0.5 mg·L⁻¹ PAM).

4. Conclusion
In this work, a new flocculation-magnetic microsphere was prepared by using the modified of Stöber method. Here, we successfully prepared Fe₃O₄/SiO₂ microspheres and achieved high response and low cost without using nanostructures as core materials. Also, the effect of different microspheres’ sizes on removal efficiency was focused on studied. Besides, Fe₃O₄/SiO₂ microspheres have no significant
reduction after at least reused five times. About 62.3% of COD, 98.3% of turbidity, 41.9 of Ni, 56.6 of Hg, and 92.4% of Pb were removed under the optimized condition. On basis of the experiment, a demonstration project project of initial road runoff treatment was designed and constructed in Tianjin, China.

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