Development of a Colloid Chemical Process for Magnetic Seeding to Organic Dye

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The recovery of organic dye molecules was achieved by using a colloidal magnetic seeding process under high-gradient magnetic separation. The recovery fraction of dye molecules was dependent on the adsorption capacity of the dye molecules. A magnetic colloid can recover a much greater amount of dye molecules than magnetite particles. The adsorption of orange Ⅱ molecules was found to be an irreversible process, and orange Ⅱ molecule could be more tightly adsorbed on a magnetic colloid than a magnetite particle surface.

The magnetic separation process for ferromagnetic materials has been used extensively in the past.[1] However, when weakly magnetic or non-magnetic particles are to be separated, a magnetic seeding process is required. The idea to employ magnetic seeding, which is usually performed by using magnetite particles with the help of a flocculant to separate weak or non-magnetic particles, is relatively new[2–6] and not yet well-developed. The magnetite particles used in the usual process of magnetic seeding so far have a relatively small specific surface area, which requires a much greater amount of particles to recover. In order to recover such materials as organic dyes with using an environmentally benign process with high efficiency, it is necessary to develop a new technique for diminishing the use of a flocculant and minimizing the added amount of magnetic particles. In general, small magnetic particles with a large specific surface area can effectively adhere to a large amount of the adsorbate, which implies that smaller magnetic particles can have the capability to adsorb a larger amount of materials. However, smaller particles, on the contrary, have a smaller magnetization, depending on the particle size. Thus, acquiring a stronger magnetic force will be needed in spite of their high adsorption capacity.

Estimates have been made of the smallest particles which could be captured on a wire by magnetic forces in competition with thermal diffusion. The smallest particle that could be captured was estimated by Kelland in 1983 to be 3 nanometers.[7] In 1983, Takayasu demonstrated the attraction of ferrofluid particles to a transversely magnetized wire, and plotted the resulting concentration gradient.[8] Gerber et al. discuss the theory of such capture by adding a magnetic term to the diffusion equation.[9] A critical particle size was found to determine whether a particle was captured in a static buildup, or became part of a concentration profile near the wire. According to these calculation results, the way for utilizing a high-gradient magnetic separation system could be opened to capture those colloidal magnetic particles which have a large specific surface area and small magnetization.

From the view point of material chemistry, Okamoto indicated that the characteristic of iron(Ⅲ) oxide colloid is a strong scavenging action which is responsible for the high specific surface area, high adsorption capacity, and strong adhesion force.[10] This indication also suggests that the use of a magnetic colloid may enable us to magnetically seed organic dyes without a flocculant.

In practice, however, the utilization of a magnetic colloid for proceeding magnetic separation could not be undertaken in those days because the technical circumstances of HGMS were not fully prepared, and a high magnetic field could not be easily produced.

In the present paper, we would like to propose a new magnetically seeding process for non-magnetic materials, called the ‘‘*colloid chemical process*,’’ and also reveal a dominant mechanism for a recovering process of organic dyes.

Experimental

1 Materials. Orange Ⅱ was used as an adsorbate for a recovery and adsorption test without further purification. Orange Ⅱ used during this work was purchased from Merck. Distilled water (specific resistivity, $\rho = 1\ \mathrm{M\Omega\,cm}$) was used during the experimental work.

The magnetic colloids were produced by a precipitation process in aqueous solution. In a typical procedure, 0.1 mol/dm^3 of iron(Ⅱ) sulfate was dissolved in 100 cm^3 of distilled water. After iron(Ⅱ) sulfate was perfectly dissolved, a 5 mol/dm^3 KOH aqueous solution was added into the prepared iron(Ⅱ) sulfate solution at a molar ratio of 1:2 for Fe:OH. Ferrous hydroxide (green rust) particles were formed just after mixing. Subsequently, the mixture solution with a suspended, $Fe(OH)_2$ precipitate was then stirred for 30 min in order to oxidize $Fe(OH)_2$ precipitates to Fe_3O_4 colloid particles by air at room temperature (25 ± 3 °C). Commercially available magnetite particles supplied by Toda Kogyo Corp. for a comparison with the magnetic colloid particles were also used.

2 Characterization of the Seeding Materials. 2.1 XRD Measurement. The oxidized products were examined by X-ray powder diffraction (RAD-R Rigaku Co., Ltd., Tokyo, Japan) with Cu Kα radiation. A colloidal sample was freeze-dried (lyophilized) and packed in a sample holder.

2.2 V.S.M. and BET Measurement. The saturation magnetization of samples was measured by V.S.M. (Vibrating Sample Magnetometer; VSM-5-15, TOEI Industry Co., LTD). About 50 mg of samples in a powder form was inserted in a capsule for magnetic measurement at room temperature. Plots of the magnetization versus the applied magnetic field were obtained directly from the instrument. The field strength was varied over a range from 0 to 20 kOe. Nitrogen adsorption isotherms were obtained at 77 K (model Gemini 2360, Shimadzu). Five data points in the relative pressure range from 0.05 to 0.30 were used to determine the specific surface area using the Brunauer–Emmett–Teller (BET) equation.

2.3 Measurement of the Particle Size Distribution. The median sizes of the magnetic colloid and commercially available magnetite particle in the suspension were determined by ultrasonic attenuation spectroscopy (Dispersion Technology, Inc., USA), as being used in the recovery and the adsorption test, because this technique enables us to measure the particle size distribution, even in high-concentrated slurries.

3 Magnetic Seeding Procedure. In order to recover dissolved orange Ⅱ molecules, commercially available magnetite particles and a prepared magnetic colloid were used to magnetically seed to the molecules. The magnetic seeding procedure adopted in this work was as follows: 100 cm^3 of an orange Ⅱ aqueous solution was placed into a 140 cm^3 polystyrene vessel. The concentration of the orange Ⅱ solution was fixed at 1.0×10^{-4} mol/dm^3. When magnetite particles were mixed into the orange Ⅱ solution, the net concentration of iron(Ⅲ) oxide in a mixed solution was changed from 60 mg/100 cm^3 to 5500 mg/100 cm^3. When the magnetic colloid was mixed into the orange Ⅱ solution, the net concentration of iron oxide particles was adjusted to the same mass on a dried-weight basis, as the case of adding magnetite particles. The calculated volume of magnetic colloid was drawn out and mixed to the orange Ⅱ solution. For this procedure, in order to maintain the orange Ⅱ concentration in solution independent of the added amount of magnetic colloid, distilled water was added to the colloid solution when a small amount of colloid was added. After mixing magnetic colloid particles or magnetite particles with the orange Ⅱ solution, the mixed solution was stirred for 2 min, and subsequently used for recovery and adsorption tests. A reason that the stirring time was fixed at 2 min is that magnetic separation should be required to be performed in as short a time as possible. All of the procedures were performed at 25 ± 3 °C, and distilled water was used above a specific resistivity $\rho = 1$ MΩ cm.

4 Recovery Test. The high-gradient magnetic-separation (HGMS) apparatus is shown schematically in Fig. 1. The magnet (Japan Magnet Technology, Inc.) has a bore of 10 cm-diameter and is 120 cm-length.

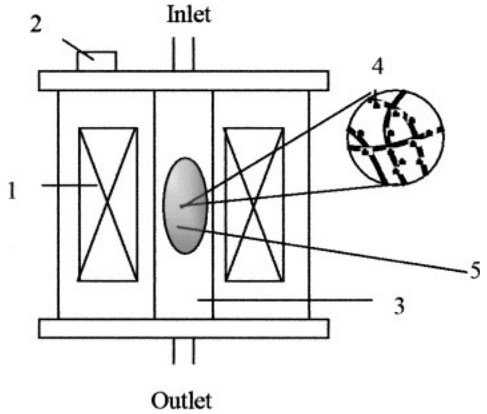

Fig. 1. Schematic of high gradient magnetic separator. 1: Superconducting magnet, 2: Refrigerator, 3: Filter canister, 4: Magnetic particle with dye molecule, 5: Stainless steel wool.

The actual HGMS column (referred to as canister) has a 4 cm inner diameter polyethylene tube and is 30 cm in length. Fresh steel wool is gently packed into a bed length of 20 cm. The stainless-steel wool has a 27 µm diameter and a weight of 6.5 g. The orange Ⅱ/magnetite solution was passed through the HGMS filter at a rate of 2000 cm^3/min to be captured on the stainless steel wool. All of the recovery experiments were performed under a magnetic field of 2 T (magnetic field gradient, 20 T/m). After the separation procedure, the absorbance (UV-240, Shimadzu, Ltd, Japan) at 485 nm through the filtrates was used to determine the recover fraction. The recovered fraction was calculated according to Eq. 1. The recovered fraction, in percentage (Recovery %), is given by

$$\text{Recovery}/\% = 100 \times \frac{A_{\text{ini}} - A_{\text{fil}}}{A_{\text{ini}}}, \tag{1}$$

where A_{ini} is the absorbance of the initial dye solution before filtration and A_{fil} is the absorbance of dye solution after filtration. Each run was repeated five times and their average value was calculated.

5 Adsorption/Desorption Test. In order to improve the recovery efficiency and increase the flow rate of the treated water to process at high speed for larger process capacities in magnetic separation, two subjects should be clarified. The first is whether the orange Ⅱ molecules are recovered by the adsorption process onto the magnetic colloid and magnetite particle surface. The second subject is whether the orange Ⅱ molecules adhere to the colloid or particles surface tightly enough so as no to be torn off when the flow rate is increased. Therefore, the adsorbed and desorbed fraction of orange Ⅱ molecules were examined, respectively.

5.1 Adsorption Test. After a prepared magnetic colloid and a magnetite particle suspension were added to 100 cm^3 of a 1.0×10^{-4} mol/dm^3 orange Ⅱ solution, the suspension was stirred while maintaining a constant agitation speed for 2 min. When a permanent magnet with 0.7 T is positioned below the vessel containing the suspension, the magnetic colloid and the magnetite particles with the adsorbed orange Ⅱ molecules are attracted to the bottom of the vessel. Three cubic centimeters of dye solution were taken from the supernatant, and its absorbance was measured, and then the adsorption fraction in percentage (adsorption %) was calculated as follows:

$$\text{Adsorption}/\% = 100 \times \frac{A_{\text{ini}} - A_{\text{s}}}{A_{\text{ini}}}, \tag{2}$$

where A_{ini} is the absorbance of the initial dye solution before an adsorption test, and A_{s} is the absorbance of the supernatant after an adsorption test.

5.2 Desorption Test. A desorption test was used to clarify the effect of the pH on the desorption of orange Ⅱ molecules from both the magnetic colloid and the magnetite particles. An adsorption test was performed as described in section 5.1, and then the particles adsorbing orange Ⅱ molecules on the surface were separated from the mixture using a 0.7 T permanent magnet. The particles with orange Ⅱ molecules were sedimented to the bottom of the bottle using a 0.7 T magnet, and the supernatant was poured out. One hundred cm^3 of solutions having different pH values from 6 to 10 were added to the each separated both magnetic colloid and magnetite particle, and then the suspensions were strongly stirred for 10 min. The pHs of the suspensions were readjusted ranging from pH 6 to 10 using a HNO_3 and KOH solution. After stirring the suspension, the suspension was taken, and its absorbance was measured. The desorbed fraction was calculated according to Eq. 3. The desorbed fraction in percentage (Desorption %) is given

$$\text{Desorption}/\% = 100 \times \frac{A_{\text{rel}}}{A_{\text{ini}} - A_{\text{s}}}, \tag{3}$$

where A_{ini} is the absorbance of the initial dye solution and A_{s} is that absorbance of the supernatant after an adsorption test; A_{rel} is the absorbance of the desorption solution.

The effect of the small amount of water involved in the separated particles was found to be small through a repeated examination; the effect was thus neglected in calculating the desorption fraction.

Results and Discussions

1 Characteristics of Magnetic Colloids and Magnetite Particles. The obtained magnetic colloid particles had a median size of 18.7 nm, a specific surface area of 57.8 m^2/g and a saturation magnetization of 37.3 emu/g. On the other hand, the characteristics of the commercially available magnetite particles has a median size of 300 nm, a specific surface area of 4.2 m^2/g and a saturation magnetization of 81.7 emu/g. If the particle shape is assumed to be spherical, the specific surface area (m^2/g) can be calculated as follows: the specific surface of each colloid particle is 1.1×10^{-15} m^2/number and that of the magnetite particle is 2.8×10^{-15} m^2/number; one can also calculate the total particle number per g of particle. Obviously, the calculated values of 51.33 m^2/g and 3.22 m^2/g are in good agreement with the measured value of 57.8 m^2/g and 4.2 m^2/g for colloid particles and magnetite particles, respectively. Since the calculated ratio of the particle diameter, based on the ratio of the specific surface area, agrees well with the ratio of the measured particle diameter, this agreement implies that both the colloid magnetic particles and the magnetite particles are not porous and have a flat and simple form of the surface. The X-ray diffraction spectra for the obtained magnetic colloid and the commercially available magnetite particle are shown in Fig. 2. The obtained XRD patterns show only the magnetite peaks for the commercially available magnetite. However, magnetite and hematite peaks appeared for the prepared magnetic colloid, though their crystallinity of phases was low. This implies that the low value of the saturation magnetization of the prepared magnetic particles may be due to the low crystallinity of the magnetite phase in the particle, and that the particle consisted of magnetite and hematite having a paramagnetic characteristic.

2 Recovery Test. A recovery test of orange Ⅱ using a magnetic colloid and commercially available magnetite particles was performed. Figure 3 shows the recovery of orange Ⅱ molecules from aqueous solution as a function of the added amount of seeding particles. Most of the adsorbed orange Ⅱ molecules were found to be recovered while passing through a stainless-steel wool filter in the super-conducting magnet. In the case of a magnetic colloid, the removal efficiency of orange Ⅱ molecules abruptly increased with an increase in the added amount of magnetic colloid.

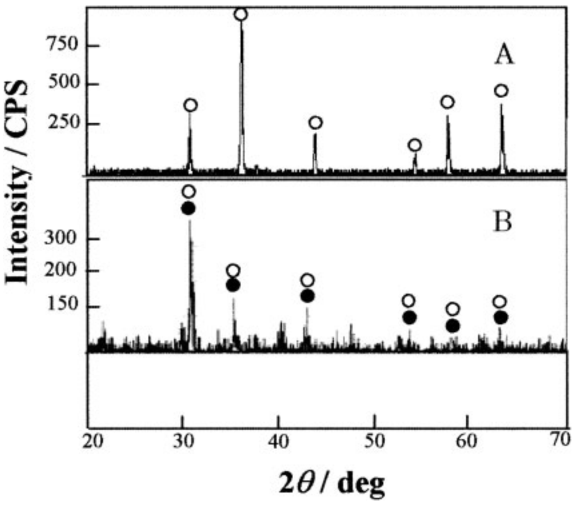

Fig. 2. XRD patterns of particles used in the experiment. (A) magnetite particle, (B) colloid particle, (○) magnetite, (●) hematite.

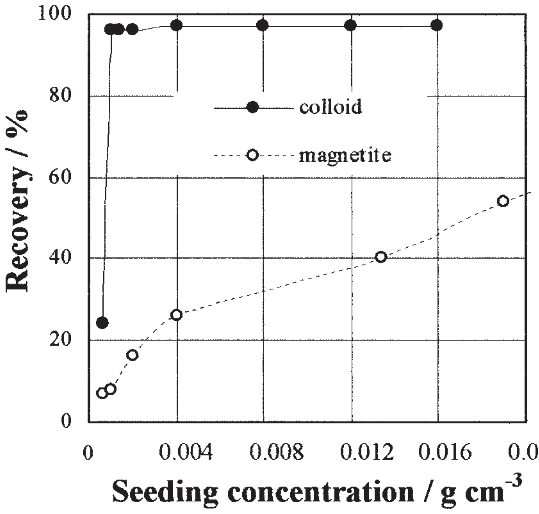

Fig. 3. Recovery of orange Ⅱ from aqueous solution as a function of added amount of magnetic seeding material.

On the other hand, orange Ⅱ molecules were removed by only about 8% at 100 mg/100 cm^3 of the added amount of magnetite particles. The recovery for the case of using magnetite particles was very low compared with the case of using a magnetic colloid. In order to remove many more orange Ⅱ molecules, magnetite particles were added further to the orange Ⅱ solution.

The recovery increased as the added amount of magnetic particle increased. When the added amount of magnetite particles reached 5500 mg/100 cm^3, a recovery of 91% was

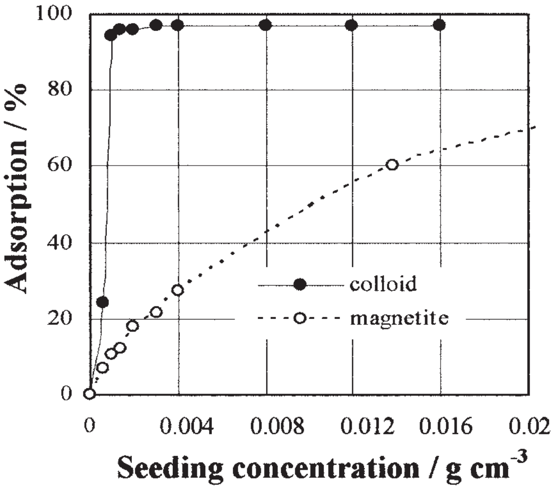

Fig. 4. Adsorption of orange II from aqueous solution as a function of added amount of magnetic seeding material.

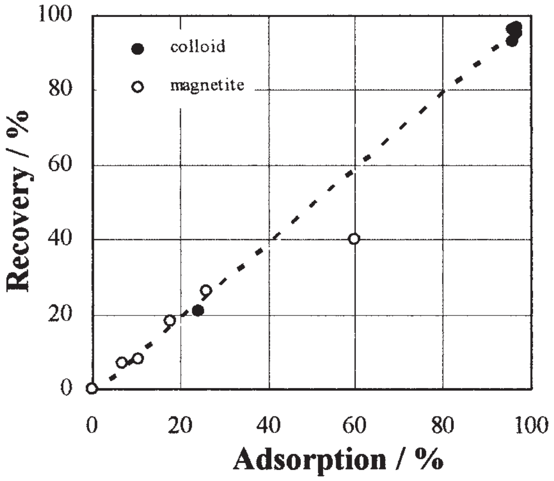

Fig. 5. The relationship of the recovery with the adsorption.

reached. Therefore, it is necessary that a large amount of magnetite particles is added to make treat an enormous volume of dye wasted water.

3 Adsorption Test. The results of an adsorption test are shown in Fig. 4. It can be seen that the adsorption of orange II molecules increased with an increase in the added amount of both the magnetic colloid and the magnetite particles. In the case of the magnetic colloid, the adsorption abruptly increased with an increase in the added amount of the magnetic colloid, the behavior of which is very similar to that of the recovery. In the case of magnetite particles, the adsorption gradually increased with an increase in the added amount of magnetite particles. This behavior was also similar with that of recovery.

4 Comparison of the Recovery with the Adsorption Behavior. An interrelation between the recovery and the adsorption behavior was examined by calculating the correlation coefficient in Fig. 5. The obtained values are very close to 1.0 for both the magnetic colloid and the magnetite particles, which indicated that 1) the recovery of orange II was responsible for the adsorption and 2) not only the magnetite particles but also the prepared colloid particles with small magnetization were captured by a magnetic filter, or magnetically enhanced sedimentation up to approximately 97% under the experimental condition employed in the present work.

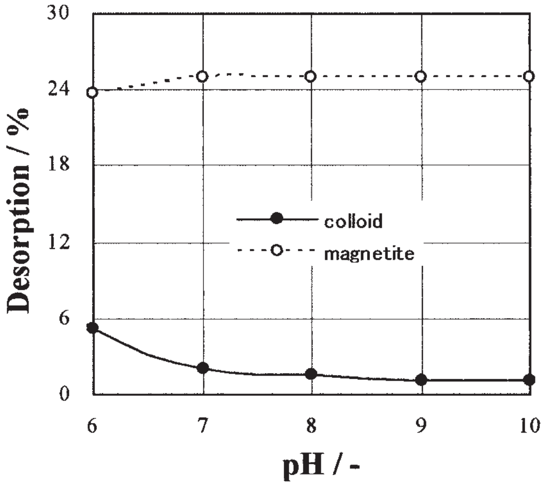

Fig. 6. Desorption of orange II from colloid and magnetite particles as a function of solution pH.

5 Desorption Test. It is expected that the flow rate of the wasted water while passing through the HGMS filter in an actual system should be much higher than that for a laboratory-scaled test, because the actual system should treat a large quantity of wasted water. In such a case, strong bonding between the orange II molecules and the magnetic particle surface is required for recovery. Thus, it is important to observe the bonding strength by performing a desorption test where the suspension of magnetic particles with the adsorbing orange II is vigorously stirred at various pH values. The obtained result of the desorption test is shown in Fig. 6. It can be seen that the bonding strength of orange II with the magnetic colloid particles is stronger than that with the magnetite particles. It can also be seen that the desorbed fraction for the magnetite particles was about 25% in the pH range from 6 to 10. On the other hand, the desorption of orange II molecules from the magnetic colloid scarcely occurred in the same pH range. This result suggested that orange II molecules were irreversibly and more tightly adsorbed on the magnetic colloid than the magnetite particles.

Conclusions

In the present study, the development of a magnetic seeding process for a non-magnetic material utilizing the characteristics of the magnetic colloid was attempted, and we proposed a new technique for magnetic seeding, called the "*colloid chemical process*".

A comparison of the results on the recovery and adsorption test revealed that the dominant mechanism for the recovering process of an organic dye is an irreversible adsorption process. The characteristics of the prepared magnetic colloid was found to have a large specific surface area with a large amount of the hydroxy group, which leads to a high adsorption capacity and a tight adhesion of the orange II molecules.

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