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The Effect of Alternative Magnetic Field on the Pigment Ejection from Magnetic Anisotropic Gel Beads

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Magnetic anisotropic gel beads (MA gel beads) were prepared by the gelation of a ferrite suspension in a static magnetic field. MA gel beads were found to oscillate in an alternating magnetic field. This oscillation can possibly reduce the thickness of the diffusion layer on the interface between the gel beads and the surrounding solution, so that the substance can be transferred more quickly across the gel-liquid interface. MA gel beads consisted of alginate gel containing ferrite powder and toluidine blue as a pigment. MA gel beads were loaded into a dual glass tube to make a column bed, which was inserted into a coreless coil which produced the alternating magnetic field. The concentration change of the pigment in the effluent from the column was measured during a lapse in time with repeating off and on the input of the alternating magnetic field. The pigment concentration in the effluent upon exposure to the alternating magnetic field increased to twice the maximum value obtained without a magnetic field. The stronger was the static magnetic field at the time of gelation and the alternating magnetic field, the larger was the increase in pigment concentration in the effluent. Also, the higher was the concentration of ferrite in gel beads, the larger was the increase in pigment concentration in the effluent.

There have been many papers concerning the utilization of gel as a carrier for the immobilization of enzymes or microorganisms.[1-3] A gel carrier is generally useful, but not efficient, if a sufficient amount of substrate can not be supplied to immobilized enzymes or microorganisms in the gel. In this case, the diffusion process of a substrate from the liquid bulk to the gel surface and that of the product from the gel to the liquid might produce the rate-determining steps. The mechanical stirring of gel beads reduces the thickness of the diffusion layer on the interface between the gel and the surrounding liquid, and increases the rate of diffusion. However mechanical stirring can possibly to break the gel beads. Although a fluidized bed was utilized, gel beads were so likely to flow out of the column bed that the flow rate of the effluent might not be sufficiently promoted for stirring.[4]

The stirring method was improved by applying a magnetic field.[4-7] Magnetite containing gel beads which exhibit a magnetic isotropic property (MI gel beads) can be moved due to an applied magnetic force. MI gel beads were reported to spin under a revolving magnetic field.[7] However, some aggregation of the beads was unavoidable in the magnetic field.[8] It seemed that the device for magnetic stirring might be a rather sophisticated instruments.[6,7]

We prepared magnetic anisotropic gel beads (MA gel beads), which exhibited a magnetic dipole like that of a magnet. MA gel beads were expected to oscillate owing to the torque, without migration or aggregation to each other in the alternating magnetic field.

This paper presents the results from a fundamental study concerning the magnetic properties of MA gel beads. Concentration measurements of the pigment diffused from inside the gel into the liquid were carried out for surveying the effects of various conditions, such as the strength of an alternating magnetic field, the concentration of ferrite powder in the gel, the size of the gel beads and the strength of the static magnetic field, in which MA gel beads were prepared.

Experimental

MA gel beads were prepared by the following method: A requisite amount of ferrite powder and 0.1 g of sodium alginate were added into 6.5 mmol dm^{-3} toluidine blue in water to make 10 g (whole weight) and mixed homogeneously (mixture A). Also, a solution of 0.1 mol dm^{-3} $CaCl_2$ in 6.5 mmol dm^{-3} toluidine blue was prepared (solution B). Into a dual beaker (inside diameter: 35 mm), 50 cm^3 of solution B were poured and kept at 25 °C. This dual beaker was placed in the center of the gap between the poles of a permanent magnet (diameter of poles: 75 mm, gap: 55—95 mm) and exposed in a magnetic field of various strengths within the range 500—1900 Oersted. Into solution B, 10 g of mixture A were added (drop by drop) by a syringe to make gel beads. These were allowed to leave over a period of 2 h in the static magnetic field. The shape of the MA gel beads became spheroid, the long axes of which were directed parallel to the flux of the static magnetic field. MI gel beads, the shapes of which were almost spherical, were prepared in the same manner, except that the dual beaker was placed far away from magnet.

Figure 1 shows a schematic diagram of the experimental apparatus. The column (inside diameter: 8 mm) was equipped with a water jacket maintained at 25 °C by circulating water. This column was surrounded with an electromagnetic coil which generated an alternating magnetic field owing to a 50-Hz alternating current. The axis of the alternating magnetic flux was set to be parallel with that of column. The column was filled with 4 cm^3 (real volume) of gel beads, producing a bed height of 9 cm^3. A gauze patch was placed at the bottom of column to hold the MA gel beads. Ten mmol dm^{-3} $CaCl_2$ was fed to the column at a flow rate of 17 $cm^3 min^{-1}$. The effluent out of column was fractionated, and each concentration of the pigment in

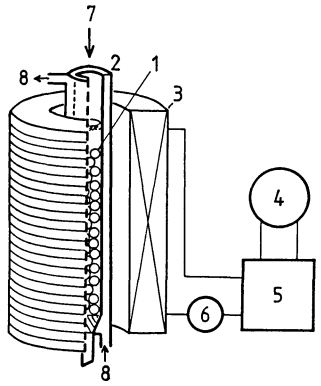

Fig. 1. The schematic diagram of equipment. 1. Gel beads. 2. Column consisted of dual glass tube for water jacket. 3. Coreless coil. 4. Electric power supply (100 V, 50 Hz). 5. Transformer. 6. a.c. ammeter. 7. 10 mmol dm^{-3} $CaCl_2$ (25 °C). 8. Circulating water (25 °C).

the effluent was determined by measuring the absorption with a spectrophotometer (Hitachi model 200-20).

In this paper we use cgs·emu as system of units and a permeability constant of, $\mu_0=1$. Therefore, the magnetic strength, H, was obtained by measuring the density of magnetic flux, B, with a Gauss meter (Yokogawa, type 3251), because $H=B$. Subscripts, s and a of H hereafter express the static and alternating magnetic field, respectively. The deviation of H_a in the column was less than 5%.

The movement of MA gel beads was observed by eye and by slow-motion video-tape.

Results and Discussion

MA Gel Beads and MI Gel Beads. Figure 2 shows photographs of the cross sections of MA and MI gel beads. Ferrite powder in MA gel beads was observed to orient along the direction of the magnetic flux. On the other hand, ferrite powder in MI gel beads dispersed without orientation.

MA gel beads were found to stick to the iron plate, having two points of each bead surface on which the magnetic flux was measured to be 10 Oersted or higher. The movement of an MA gel bead in water was observed in the alternating magnetic field. The bead was observed to leap. This motion was examined with slow-motion video-tape, showing MA gel beads which did not follow the 50-Hz field: At a magnetic strength of 200—500 Oersted, the long axes of the MA gel beads were observed to be at right angles to the magnetic flux, and oscillated at an angle of several to 10 and more degrees. They occasionally rotated to the long axis of the MA gel bead. These results suggest that MA gel beads might possess magnetic poles and a magnetic moment like a magnet.

MI gel beads, on the contrary, exhibited neither magnetic attraction to iron plate in a non-magnetic field nor oscillation under an alternating magnetic field.

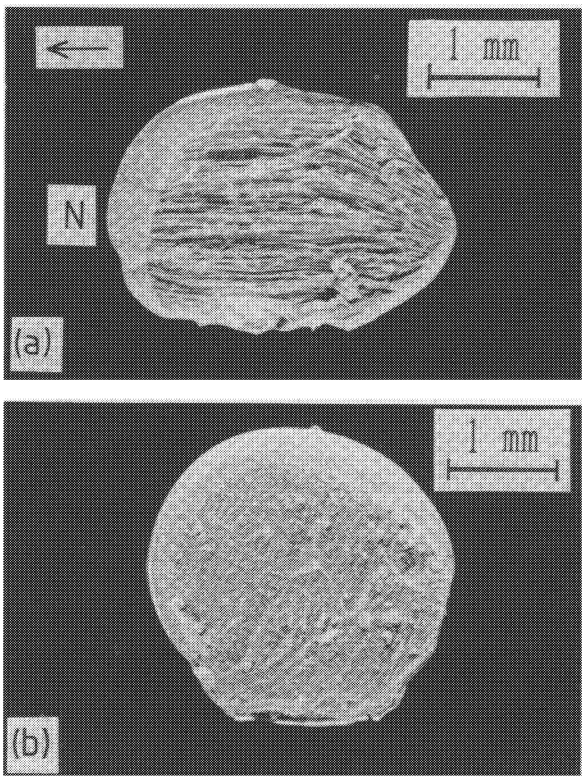

Fig. 2. Photographs on cross sections of an MA gel bead and an MI gel bead. (a): An MA gel bead, which contained 5% ferrite and was prepared in H_s=1600 Oersted. The direction of magnetic flux is shown by an arrow. N and S show north and south as both poles of a bead. (b) An MI gel bead, which contained 5% ferrite and was prepared in H_s<0.5 Oersted.

The Diffusion Rate of Pigment from MA Gel Beads. MA or MI gel beads filling the column were exposed to the alternating magnetic field. The concentration change of toluidine blue as pigment in the effluent was determined. The results are shown in Fig. 3. The concentration of toluidine blue in the effluent gradually decreased with a lapse of time, and increased only when MA gel beads were exposed to the alternating magnetic field. No concentration change of toluidine blue occurred in the case of MI gel beads.

It should be noticed that the surface area of the MA gel beads might not change, since these beads did not transform under a magnetic force in the magnetic field. Meanwhile, the rate of the efflux was kept constant. Therefore, it is reasonable that only the rate change of molecular transfer across the interface between the surface of the gel beads and the liquid bulk may exert to the concentration change of toluidine blue in effluent. The oscillation of MA gel beads may cause a decrease in the thickness of the diffusion layer on the interface between the surface of the gel beads and the liquid bulk, and to increase the concentration of toluidine blue in the effluent.

The Factors Influencing on Efflux of Pigment from MA Gel Beads. The effects of the strength of the

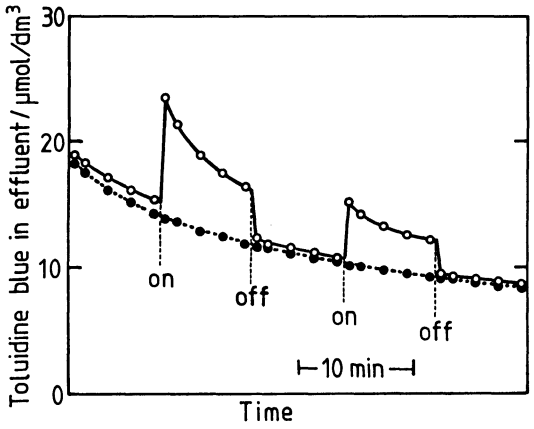

Fig. 3. The concentration change of pigment in effluent by exposing alternating magnetic field off and on. MA gel beads (—○—) prepared in H_s=1600 Oersted and MI gel beads (—●—) prepared in H_s<0.5 Oersted. H_a=600 Oersted. Ferrite concentration in gel beads: 5%. Average diameter of gel beads: 2.7±0.3 mm.

alternating magnetic field (H_a), the concentration of the ferrite powder in the gel, the size of the gel beads and the strength of the static magnetic field (H_s) for producing MA gel beads on the concentration change of the pigment in the effluent were surveyed.

Figures 4, 5, 6, and 7 show the results concerning the concentration change of toluidine blue in the effluent with a time lapse under various conditions. It was found from the inserted figures in Figs. 4—6 that the ΔC_s (the values of subtraction of the toluidine blue concentration before and after exposing magnetic field) are almost proportional to H_a, the size of the gel beads and the concentration of the ferrite powder, respectively. Figure 7 shows that no change appeared below 500 Oersted. It seems that ΔC may be proportional to H_s as a function of the second degree in the region above 500 Oersted in the inserted figure in Fig. 7. These results suggest that the static magnetic field might be the most effective factor concerning the concentration change of the pigment in the effluent.

The magnetic force from both poles in the gap of magnet to ferrite powder inside the gel caused the shape of MA gel beads to be slightly ellipsoidal. This fact was more clearly observed at higher H_s.

The magnetic moment of MA gel beads is produced by the orientation of ferrite powder inside the gel parallel to the direction of the magnetic flux. It seems that the more the NS poles of each ferrite particle of powder are forced to orient parallel to the magnetic flux with elevating H_s, the more the magnetic moment of MA gel beads increases. Also, the magnetic moment may increase with increasing the size of the MA gel beads. The magnetic moment of MA gel beads brings about a torque which is the product of H_a and the magnetic moment of the gel

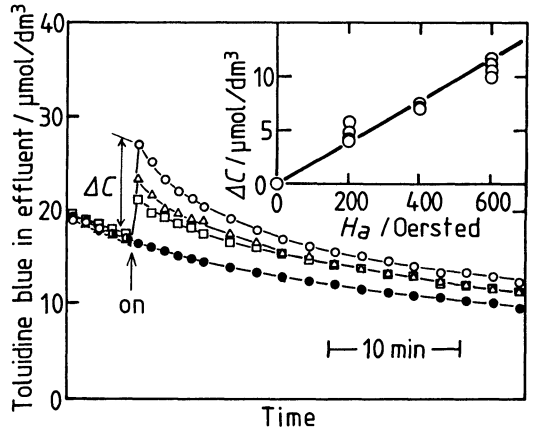

Fig. 4. The relation between ΔC and H_a. H_a=600 (—○—), 400 (—△—), 200 (—□—), and 0 (—●—) Oersted. Other conditions were the same as those in Fig. 3.

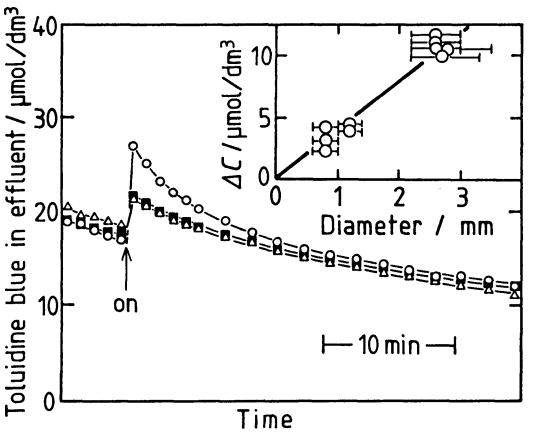

Fig. 5. The relation between ΔC and the size of average diameters of gel beads. Gel beads diameter were 2.6 (—○—), 1.2 (—■—), and 0.8 (—△—) mm. Other conditions were the same as those in Fig. 3.

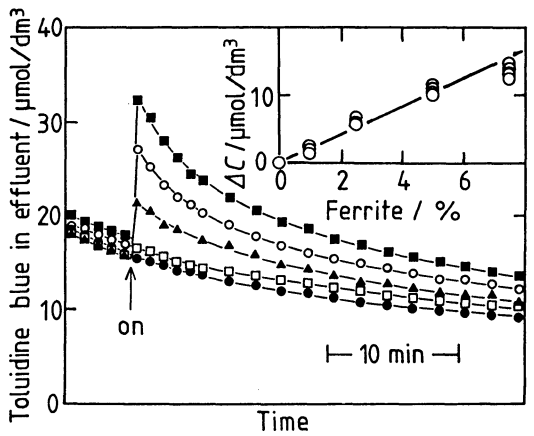

Fig. 6. The relation between ΔC and ferrite concentration in gel. Ferrite concentrations: 7.5 (—■—), 5.0 (—○—), 2.5 (—▲—), 1.0 (—□—), and 0 (—●—) %. Other conditions were the same as those in Fig. 3.

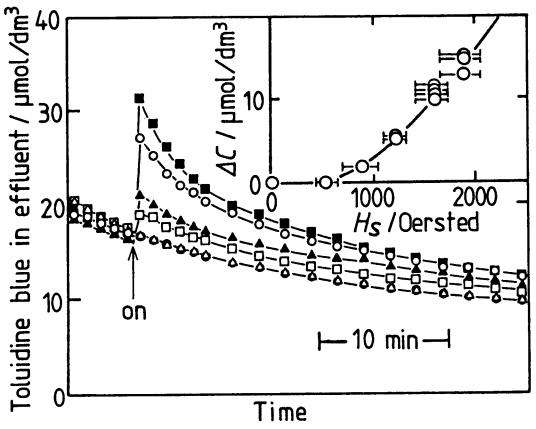

Fig. 7. The relation between ΔC and H_s. H_s=1900 (—■—), 1600 (—○—), 1200 (—▲—), 900 (—□—), 500 (—●—), and 0 (—△—) Oersted. Other conditions were the same as those in Fig. 3.

beads in the magnetic field. MA gel beads oscillate owing to the torque. It is plausible that the diffusion layer on the surface of gel beads reduces the thickness by intensifying the oscillation of MA gel beads. In order to obtain ΔC. H_s has to be pushed up more than 500 Oersted in Fig. 7. This fact indicates the existence of a threshold: The magnitude of the torque must overcome the frictional resistance caused by the thrust of MA gel beads on each other. In this connection, the oscillation can prevent the aggregation of gel beads with each other.

Conclusion

It was demonstrated that MA gel beads prepared in a static magnetic field oscillated due to the torque produced by an alternating magnetic field. The oscillation of MA gel beads promoted the velocity of pigment ejection from the inside gel beads to the liquid bulk, as compared with no alternating magnetic field. This is different from the behavior of MI gel beads in a magnetic field. It is obvious from Figs. 2 and 4—7 that (1) the orientation of magnetite powder in gel in the static magnetic field yields the magnetic moment. (2) the magnitude of the magnetic moment of MA gel beads varies as the concentration of ferrite powder in the gel, the size of MA gel beads and H_s for gelation, and (3) the magnitude of the torque of MA gel beads increases with increasing H_s. We discussed this phenomena in this paper. A theoretical analysis of the relation between the oscillation and the magnetic moment of MA gel beads will be presented in a separate paper.

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