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journal or publication title	Research journal of chemistry and environment
volume	10
number	2
page range	7-13
URL	http://hdl.handle.net/10232/00003206

The new hybrid ceramic beads synthesized from natural minerals and titanium dioxide for the waste water cleaning

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Abstract

Porous hybrid ceramic beads were synthesized by burning at 1090°C under a reductive atmosphere. They consist of the natural mineral (graphite silica, GS), the pyroclastic deposit “shirasu” and titanium dioxide. They showed the bleaching of the aqueous dyestuff solutions (rhodamin B, acridine orange, methyl orange, methylene blue) and the degradation of a surfactant dodecyltrimethylpyridinium bromide and humic acid. The decolorizing rate of dye stuff was monitored by the absorption spectra under UV irradiation and a dark condition. The repeatedly reused ceramic beads also proved a comparable performance to the new ceramic beads for decolorizing of dye solution. The rate was compared for some ceramic beads of different components and structures. The effect of anatase titanium oxide on the ceramics surface and the UV irradiation was not clear. These ceramic beads were applied for the decolorizing of cattle urine pretreated by microorganisms and proved the high performance.

Key Words: Water processing, Waste water, Catalysis, Dye degradation, Hybrid ceramics

Introduction

Water is essential to all creatures as well as human being. Clean water has been recycled by the natural circulation via vaporization from ocean and rain. However, the severe water pollution has been recently produced from waste water of human activity by its very quick growth and many academic journals have been published to discuss and develop the solution of the water pollution¹⁻⁸. Therefore, reuse and recycle of waste water is the urgent subject to human being.

Various water processing materials has been developed. They include coagulants, flocculants,

adsorbents, oxidizing agents, photocatalysts, and so on⁹⁻²⁹.

Waste water from dyeing industries, urine of livestock farmers, chemistry industries, etc. deeply colored and the water is often still colored after a proper primary water processing. We developed a new water processing material “Taiyo” to decolorize completely the water output after primary water processing such as treatments by microorganism, flocculants, oxidation, etc. This paper will present the results of trial examination.

Material and Method

Materials : Graphite silica (GS) was obtained

from Heiseikaminokuni Mines (Hokkaido) and used as jet milled powder of $\sim 5\ \mu\text{m}$. A well defined “shiras” powder of $\sim 5\ \mu\text{m}$ by elutriation was obtained from Seishin Industry (Kagoshima). Titanium dioxide powder (P25, Degussa) was purchased from Nippon Aerosil (Yokkaichi). Titanium dioxide sol was obtained from Tiotechno. The dyes, rhodamine B (RB, Kanto Chemicals), methyl orange (MO, Wako), methylene blue (MB, Nakarai), acridine orange (AO, Aldrich), were used as received. A surfactant dodecyltrimethylammonium bromide (DPy, Wako, GR) was also used. Humic acid was extracted from crude HA piled up in Heilungkiang, China (MSHA) by the IHSS recommendation method.

Synthesis of hybrid ceramic beads for water processing : Four water processing beads were synthesized. Firstly, GS and “shirasu” was mixed and the beads were made using flour as a binder. The beads were dried and then burned under the reductive atmosphere in a furnace for 5 h. The temperature elevation to 1090°C took 5 h. The cooling to 300°C was carried out under nitrogen atmosphere in the furnace for 60 h (T0). The dried beads of pre-burned T0 were covered with the mixed powder of GS, “shirasu” and P25 by using flour as the binding and then burned under the reductive atmosphere at 1090°C . Again the cooling was carried out under the nitrogen atmosphere and the core-shell type beads were obtained (T1). In this burning condition TiO_2 changed the titanium nitride. XRD measurement revealed the rutile TiN on the bead surface. The T0 ceramic beads were covered with P25 powder and burned under the oxidative atmosphere at 450°C (T2). The outer shell of T2 was composed with anatase TiO_2 . The T1 ceramic beads were coated with TiO_2 sol and burned at 450°C (T3). The composition of the hybrid

ceramic beads was given in Table 1.

Decolorizing measurements : About 10 g of ceramic beads were added to 50 ml dye solutions. The absorbance of the dye solutions was adjusted to be 1 at the wavelength of band peak in the absorption spectrum. Two vials of the same solution were prepared and the one was rapped with aluminum foil to prevent from the UV irradiation. All the vials were irradiated by black light (Toshiba FL20S BLB) 30 cm above from the vials. The Pyrex glass shows 90% transmittance at 350 nm where the black light gives the maximum irradiation power.

Results and Discussion

Decolorizing of dyes. Figure 1 shows the time dependence of RB spectrum in the presence of T1 ceramic beads. Few T1 ceramic beads (ca. 5 g) were added to a 50 mL of 0.02 mM RB solution. Decolorizing is clearly shown in both runs, under the UV irradiation (A) and in the dark (B). The time dependence of absorbance at the peak wavelength 553 nm was compared (Fig. 2). No decolorizing was observed in the absence of T1 ceramic beads (c), while T1 ceramic beads contribute to decolorize RB solution. UV irradiation seems to accelerate the decolorizing of RB (a), but the comparable decolorizing is still observed without UV irradiation (b).

Decolorizing of some dye solutions, AO, MO and MB was examined under the irradiation and in the dark condition at an increased feeding of T1 ceramic beads (5 g T1 in a 15 mL dye solution). The dye concentrations were determined as 0.07 mM for AO, 0.2 mM MO and 0.05 mM MB, so that the starting absorbance was about 1 at the wavelength with the maximum absorbance in the band (491nm for AO, 464nm for MO and

664nm for MB). In the absence of T1 ceramic beads no degradation was observed in MO solution (a, open marks), while a little degradation was observed in AO and MB solutions (b and c, open marks), indicating the stability of the dye solutions. The T1 ceramic beads show the remarkable effect on the degradation (solid marks). The residual absorbance was under 20% at 2 h at the both conditions, UV irradiation and no irradiation.

Since Fig. 3 suggests a little difference between the UV irradiation and the dark condition, the degradation curves were compared in Fig. 4. Figure 4 indicates that the UV irradiation had no or a little less effect on the decolorizing of the dye solutions. The titanium in the T1 ceramic beads was confirmed to be titanium nitride of rutile form by powder XRD measurement, because the ceramic was burned at 1095°C under the reducing atmosphere. Even if the T1 ceramic beads include the titanium oxide, the rutile form has no photocatalysis. This could be reason why the irradiation had no effect. However, we have to take into account the adsorption effect of T1 ceramic beads.

Adsorption reaches the saturation in the high solute concentration. The repeated use of adsorbent may cause a deterioration of the adsorbent and a slow decolorizing of dye solutions. Figure 5 indicates the decolorizing of AO and MB solutions by the fresh and the five times reused T1 ceramic beads. Reusing of T1 ceramic beads did not cause any deterioration of decolorizing effect. This fact suggests the dye decomposition catalyzed by the T1 ceramic beads.

In order to reveal the adsorption effect by “Taiyo” ceramic beads, the T1 powder were examined for the decolorizing of RB. Figure 6 shows time dependence of RB absorbance in

the presence of T1 ceramic powder and silica gel powder as a reference. The absorbance reaches minimum after 30 minutes and shows no decreasing any more. On the other hand, T1 ceramic beads showed a slow decrease up to 2 h, but kept the absorbance decreasing and reached at absorbance 2.35 after 2 days that is comparable to the absorbance by T1 powder. After 1 month, the complete decolorizing of RB was observed in the presence of T1 ceramic beads, but the RB color was still left in the solution including T1 ceramic powder and silica gel powder. These facts point at an adsorption of RB by T1 powder and the degradation of RB by T1 ceramic beads.

Missing amount of RB was plotted against the concentration of BR left in the solution after 8 h in Fig. 7. The data were obtained at the condition of 0.1 g powder in 5.0 g RB solution. When missing amount was ascribed to the adsorption by the powders, Fig. 7 corresponds to the binding isotherms (the plot of the adsorbed amount of RB versus the equilibrium concentration of RB, C_f). All the curves taken at different times (30 min, 1 h, 5 h and 8 h) agreed with each other within the experimental error. The saturation amounts of RB by T1 ceramic powder are much less than that by the silica gel, but the adsorption constant, that can be estimated from the slope at the origin in the curve, was much larger for T1 powder than for the silica gel. The curves at low equilibrium concentration of RB (inserted figure in Fig. 7) indicated nearly complete adsorption of RB. These curves for T1 ceramic powders do not fit to the Langmuir equation.

The surface fluorescence by adsorbed RB was measured for the T1 and silica gel powders. No emission was observed for T1, but the silica gel powder showed the fluorescence as well as orange color. The facts that the binding curves

and the surface emission by the T1 and T0 ceramic beads are very different with those by the silica gel powder suggest the degradation of RB.

Comparison of the “Taiyo” ceramic beads.

The degradation rates of some dyes were compared for the four “Taiyo” ceramic beads. Four “Taiyo” ceramic beads were synthesized (Table 1). Their activity for the degradation of AO, MO and MB were compared both under the UV irradiation and the dark condition. Since the T2 and T3 ceramic beads were covered by TiO_2 and burned at 450 °C, the photocatalysis anatase TiO_2 is expected to cover the bead surface. The test solutions contained 5 g ceramic beads in the 15 mL dye solutions. The dye concentrations were 0.07 mM for AO, 0.2 mM for MO and 0.05 mM MB and the absorbance at the peak wavelength was adjusted around 1.0 for all dye solutions. The absorbance was monitored at 490 nm for AO, 463 nm for MO, and 664 nm for MB. The 90% bleaching was observed within 8 h for the all ceramic beads. The initial rate was given in Table 2. The T2 and T3 ceramic beads do not promote the degradation of the dyes even under the UV irradiation. The T1 ceramic beads under UV irradiation are most effective to bleach the dye solutions among the four “Taiyo” ceramic beads.

Degradation of surfactant, dodecylpyridinium ion (DPy), and humic acid (HA) was examined. The initial bleaching rates were given in Table 3. The DPy concentration was 0.50 mM and the absorbance was monitored at 258 nm. The bleaching rate is smaller for DPy than for the dyes and it took 10 h for 75% bleaching. Since HA had no absorption maximum in visible region, the bleaching of HA were monitored at 560 nm. HA was extracted in alkaline solution from the

sediment of decomposing terrestrial vegetation in ancient times. HA contains some sort of chelating groups to help stabilize the transition metal ions in solution and causes the contamination of underground water by the metal ions. The degradation of HA is quite important for the clean water sources. The HA degradation by “Taiyo” was found to be very slow as shown in Table 3 due to the very stable organic compound. Among the four ceramic beads T1 and T3 were effective for the HA bleaching both under the UV irradiation and the dark condition.

The results in Tables 2 and 3 as well as in RB bleaching indicate (1) no remarkable effect of T2 and T3 and (2) a comparable effect of T0 for the degradation of dyes and a surfactant. (3) Light brown T1 ceramic beads and the powder were synthesized by the oxidative burning over 1000°C and proved no bleaching effect on the dyes. Since T2 and T3 were covered with TiO_2 powder or the colloid solution and burned at 450°C, the photocatalyst anatase TiO_2 was formed on the surfaces. The non-preponderance of T2 and T3 under the UV irradiation points at no responsibility of photocatalysis to the dye degradation. The T0 and T1 ceramic beads were composed of GS and “shirasu” but no anatase TiO_2 and they still have the bleaching effect on the dyes. However, the fact that the light brown T1 beads and powder by the oxidative burning had no bleaching for the dyes points at the key role of graphite component in GS. T1 beads were somewhat predominant for the degradation.

From these results we speculate the mechanism of the hybrid ceramic beads catalysis. GS contributes the quick adsorption, but the saturation amounts are small (Fig. 7). The slow degradation of organic compounds occurs at a polycrystalline boundary of GS and

TiN inside of the beads. The graphite in T1 powder contributes only to the strong RB adsorption on the surface which specific area is expected larger than the T1 bead surface, but much less than the porous silica gel. The small specific area was expected from the SEM image that shows an elaborate surface of a T1 bead presumably due to the glassy components of "shirasu". This property of T1 powder leads to the small saturation and the quick and sharp adsorption at low RB concentration. The strong adsorption leads to a difficult release of the degraded products and interferes the successive adsorption.

The livestock urine is treated by microorganisms and is drained to rivers and seas. However, the microorganism treatment is not perfect and the waste water is still colored. The T1 ceramic beads were applied to the water discharge after primary treatment by microorganisms. A miniature system was constructed and the bleaching was tested. The system consisted of five tubes filled with 40 liter T1 beads and the waste water run through the tubes. The water output after the second tube showed no color and the final water output was used for feeding gold fishes. Figure 8 shows the photo of the system. Gold fishes have been alive and grown in the fish tank of waste water for 8 months.

Conclusion

The new hybridized ceramic beads were synthesized from the natural minerals, graphite silica and shirasu, and TiO₂. They showed an excellent property for decolorizing some organic solutions. The adsorption capacity was not high, but the complete breaching was after a long period. The facts indicate the degradation of organic compounds catalyzed by the ceramic beads. The ceramic beads were applied to the decoloration of deep-colored

water output from the primary treatment of livestock urine and gold fishes have been alive for 8 months. Thus, these new hybrid ceramic beads are excellent for water processing.

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Table 1. Composition of the hybrid ceramic beads

Ceramic Beads		Composition	Calcination
B-MS (T0)		GS 60%, Shirasu 40%	1095°C, Reductive
B-T1 (T1)	Core	GS 20%, Shirasu 80%	1095°C, Reductive
	Shell	GS 40%, Shirasu 40%, P5 20%	1095°C, Reductive
B-T2 (T2)	Core	GS 60%, Shirasu 40%	1095°C, Reductive
	Shell	P5	450°C, Oxidative
B-T3 (T3)	Core	GS 20%, Shirasu 80%	1095°C, Reductive
	Shell	GS 40%, Shirasu 40%, P5 20%	1095°C, Reductive
	Surface	TiO ₂ sol sprayed	450°C, Oxidative

Table 2. Initial rate of bleaching reaction in the presence of “Taiyo”.

” Taiyo”	Unit: $\Delta\%/h$					
	AO		MO		MB	
	UV	Dark	UV	Dark	UV	Dark
T0	0.52	0.38	0.37	0.27	0.38	0.36
T1	0.57	0.41	0.55	0.49	0.55	0.30
T2	0.39	0.39	0.35	0.34	0.43	0.36
T3	0.35	0.39	0.31	0.34	0.38	0.39
None	0.08	0.09	0.01	0.01	0.03	0.03

Table 3. Initial rate of bleaching reaction in the presence of “Taiyo”.

Taiyo	Unit: $\Delta\%/h$			
	DPy		HA	
	UV	Dark	UV	Dark
T0	0.29	0.23	0.05	0.05
T1	0.33	0.23	0.13	0.08
T2	0.31	0.27	0.02	0.03
T3	0.30	0.26	0.09	0.09
None	0.02	0.00	0.01	0.01

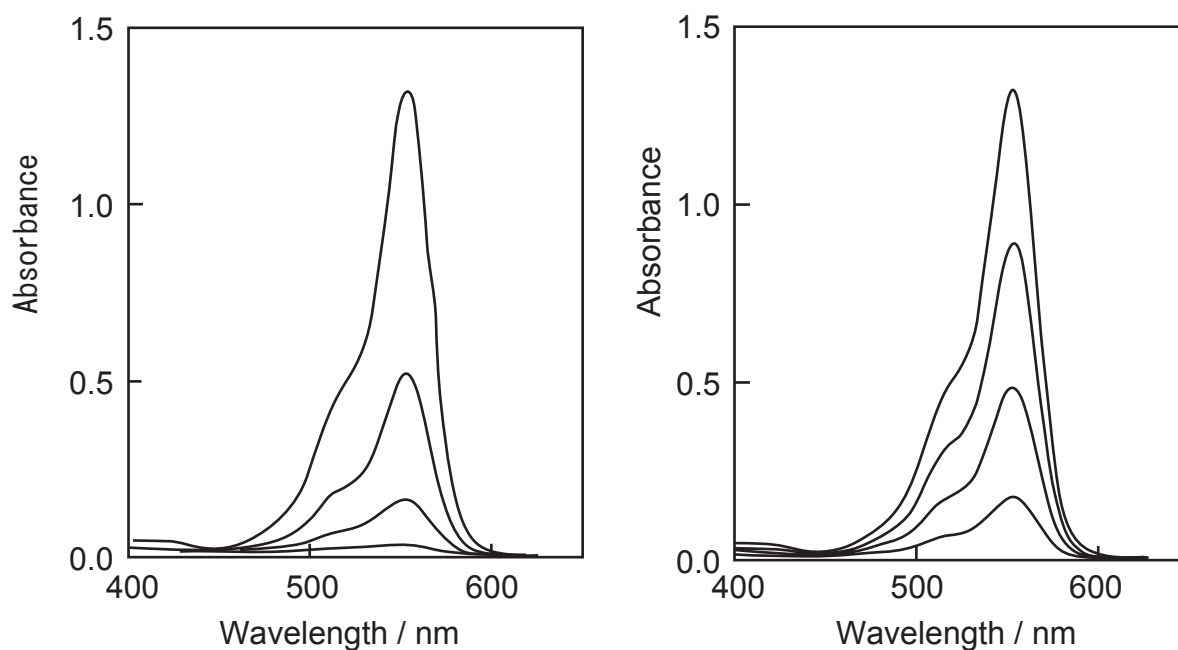


Fig. 1. The absorption spectra of RB in the presence of T1 under the UV irradiation (A) and the dark condition (B) at different times. Time (top to bottom): 0, 1, 2, 3 d.

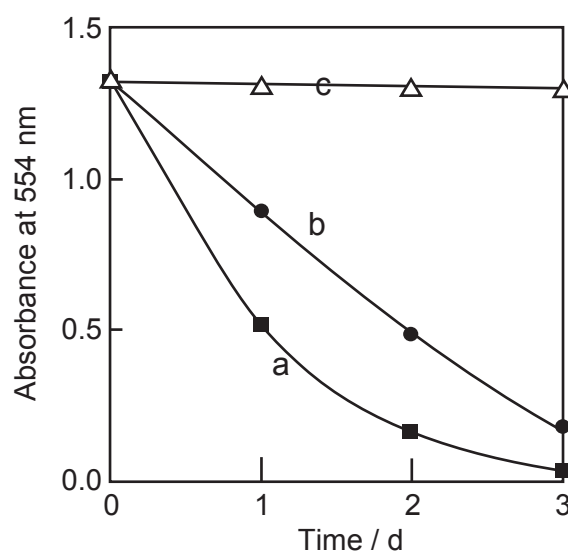


Fig. 2. Time dependence of the absorbance at 554 nm in the presence of T1 under the irradiation (a), dark condition (b), and in the absence of T1 under the UV irradiation (c)

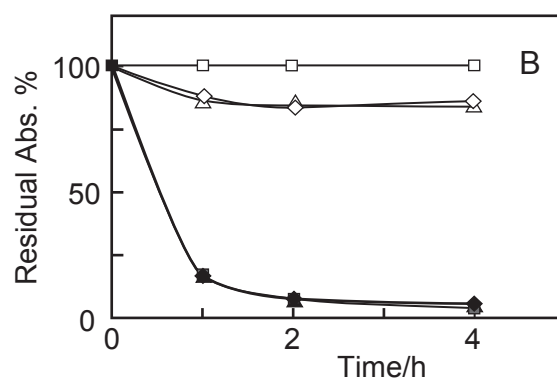
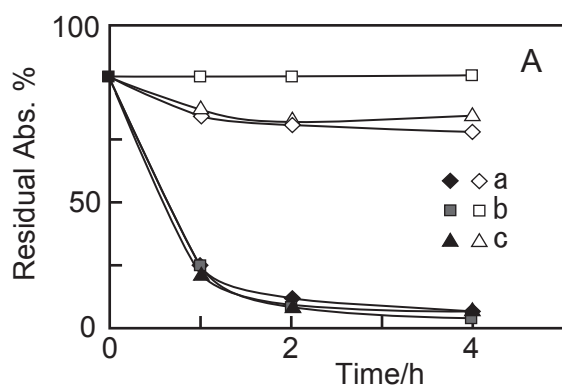


Fig. 3. Bleaching of dye solutions by T1 under the UV irradiation (A) and dark condition (B) at a room temperature. a. AO, b. MO, c. MB; solid marks: 5 g T1 in 15 mL dye solutions and open marks: no T1.

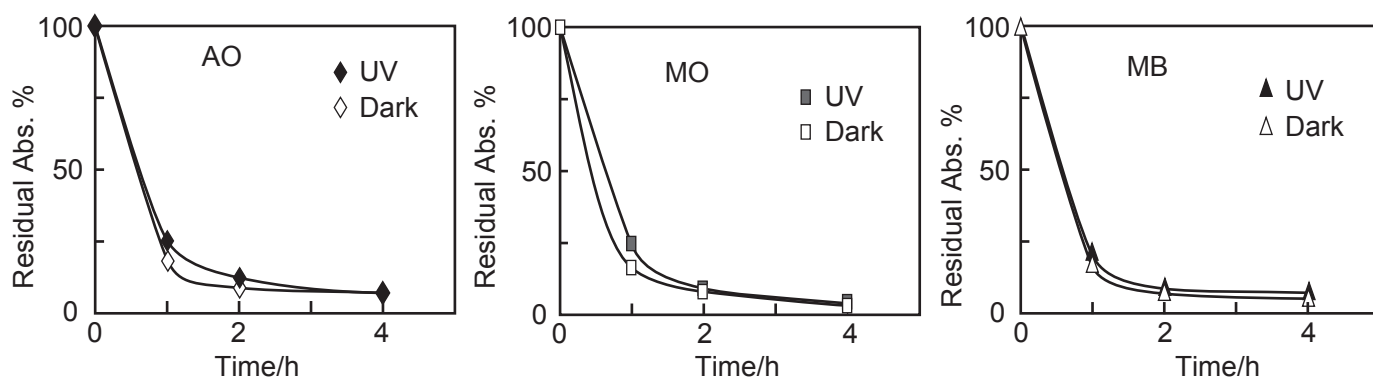


Fig. 4. Comparison of the bleaching curves under the UV irradiation (solid marks) and the dark condition (open marks) in the presence of 5 g in 15 mL dye solutions (0.07 mM AO, 0.20 mM MO and 0.05 mM MB).

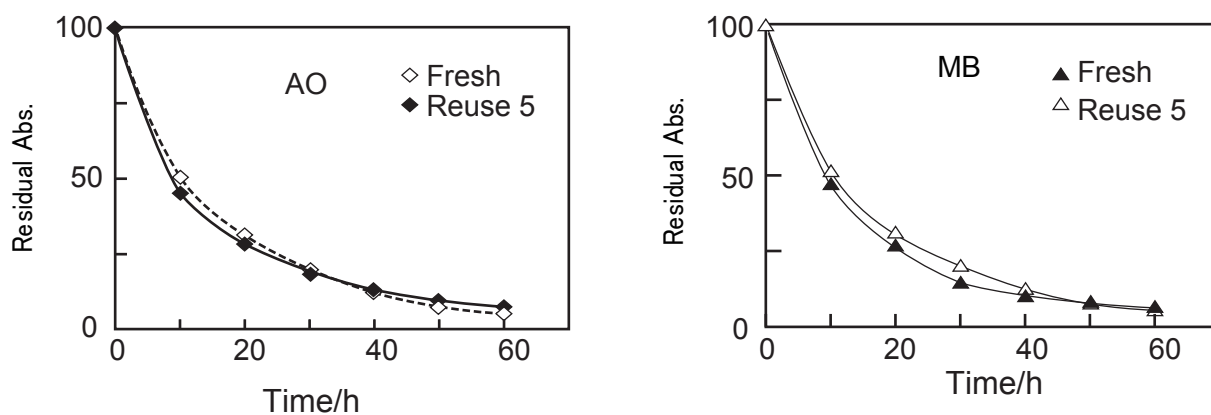


Fig. 5. Comparison of the bleaching of AO (A) and MB (B) by the fresh T1 (solid marks) and by the T1 reused five times (open marks) under the UV irradiation at room temperature. 5 g T1 was used in 15 mL dye solution.

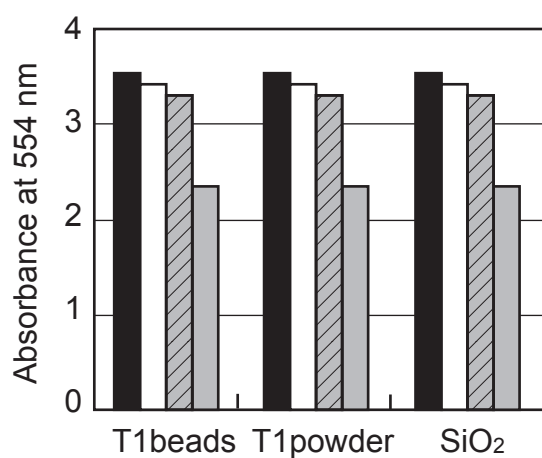


Fig. 6. Comparison of breaching of RB by the T1 beads, T1 powder and silica gel powder at different times.

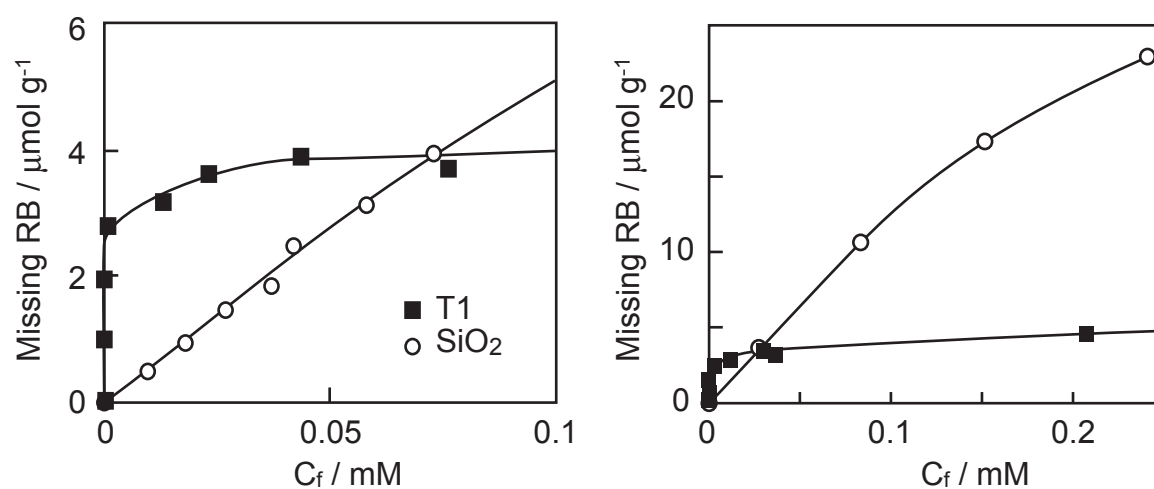


Fig. 7. Dependence of the missing RB on the equilibrium concentration in the presence of T1 (solid squares) and silica gel powders (open circles). A: high RB concentration region.

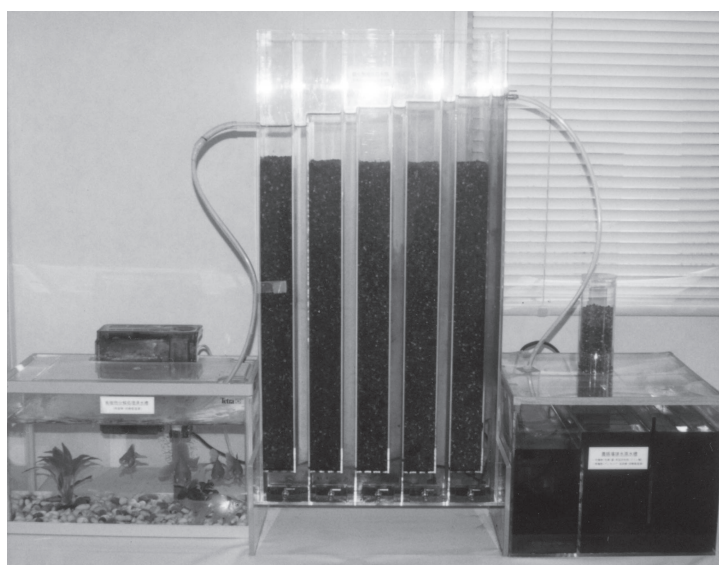


Fig. 8. The miniature apparatus of the water processing system for waste water from livestock urin.