USING CARBONIZED REFUSE DERIVED FUEL TO RESTORE SEAWEED FORESTS: A POTENTIAL CONSERVATION TECHNIQUE

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Abstract. We have recently developed a new material by carbonizing refuse derived fuel (RDF) not discharging dioxin and other toxic fine particles. This recycled carbonaceous material (CRDF) has two major good points: 1) rich in the three chemical elements of fertilizer (nitrogen, phosphoric acid and potassium) and 2) a good adsorbent like activated charcoal. In this study, making the best use of these merits, we looked into the possibility of using this material to restore seaweed forests that were damaged by human activities. We confirmed that no toxic substance was liquated out from this material. In the laboratory experiments, the growth of a species of marine green algae (*Derbesia tenuissima* (Moris et De Notaris) Crouan) was accelerated by this material. CRDF might supply nitrogen short in seawater as the form of nitrate. Our technique was actually effective to introduce marine algae in the fields using a series of test plates that included this material ranging from 0 to 8.2 % (w/w). We might not only recover biodiversity in coastal ecosystems by restoring seaweed forests but also remarkably reduce atmospheric CO_2 released in the process of the incineration of waste with this technique.
Keyword: *atmospheric CO_2, biodiversity, coastal ecosystems, carbonaceous material, water pollution*

Introduction

Refuse derived fuel (RDF) is produced from municipal solid waste (MSW) through following processes: separating at source; sorting or mechanical separation; size reduction (shredding, chipping and milling); separation and screening; blending; drying and palletizing [3]. The waste material is screened to remove the recyclable fractions (e.g. metals), the inert fractions (e.g. glass) and the fine wet putrescible fractions (e.g. food) before being pulverized. The calorific power of RDF is approximately 5000 kcal kg^{-1}, which is similar to that of coal. RDF is often used to generate electricity. In Japan, however, since a serious accident at an electric power plant using RDF in Mie prefecture in 2003, the demand of RDF is decreasing. It would be, therefore, important to find another way to use RDF effectively and safely.

We have recently developed a new carbonaceous material with RDF. In the producing process, we pyrolyze RDF without oxygen at a very high temperature (>1000˚C), so dioxin and other toxic gasses are not produced. We can also use thermal energy left over in the iron manufacture processes not to generate additional CO_2. By carbonization, the weight of waste is decreased by ca. 12.5 %. We call this material CRDF. We found that CRDF has some chemical and physical good points. First, it is rich in the three chemical elements of fertilizer (i.e. nitrogen, phosphoric acid and potassium). In our preliminary research, these percentages are 1.7, 3.0 and 1.1 % (w/w), respectively. Second, it is a good adsorbent like activated charcoal. This appears to be due to a large surface area (i.e. 140 m^2 g^{-1} in our preliminary research).

The inshore fishery is one of very important industries in many countries including Japan. Fishery products have been key sources of food since early times, constituting 20% of the Japanese people's protein consumption (see the Japanese government annual report on the fisheries at http://www.maff.go.jp/eindex.html). Many commercially important fish populations, however, have been declining in the past several decades [5, 10]. One of the major reasons for decreasing fisheries is destruction of seaweed forests by human activities. Seaweed forests play significant roles in maintaining biodiversity of coastal marine ecosystems (e.g. [7]). Marine algae are not only foods for herbivores, but also provide spawning and hiding places for juveniles of many marine organisms. For instance, settlement and germination of seaweed spores are seriously disturbed by species of coralline red algae (e.g. [6] for *Lithophyllum yessoense* Foslie), which is exacerbated by human activities (see [8]). In this study, we carefully examine whether CRDF could be used to solve these crucial environmental problems restoring seaweed forests.

Materials and methods

Scanning electron microscope observations

The surface ultrastructures of the carbonaceous material were observed using a scanning electron microscope (SEM, Hitachi S-2050). We prepared a series of samples varying the proportion of the carbonaceous material (i.e. 3, 20 and 90 % w/w) using starch as a binder.

Eluent test

We checked whether 24 chemical compounds were eluted from CRDF: alkylmercury, organic mercury, inorganic mercury, cadmium, lead, organophosphorus, chromium 6, arsenic, total cyanide, poly chlorinated biphenyl, trichloroethylene, tetrachloroethylene, 1,2-dichloroethane, 1,1-dichloroethylene, cis-1,2-dichloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,3-dichloropropene, thiuram, simazine, thiobencarb, benzene and selenium. Such tests are necessary for materials made from municipal solid waste (MSW). For the metals, Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used and a Mass Spec was used for the rest.

Laboratory study

Materials

We used male gametophytes of a dioecious marine green alga, *Derbesia tenuissima* (Derbesiaceae) in our laboratory experiments. They usually do not branch out (*Fig. 1*; [16]). We safely estimated their biomass (volume) assuming the shape of each gametophyte as ellipsoidal (volume (V) = $4/3\ \pi ab^2$, a: radius on the minor axis; b: radius on the major axis) [4], and easily and correctly measured the growth rate of this alga. We used only male gametophytes because female gametes parthenogenetically develop into filamentous sporophytes. For each culture experiment, we prepared even-sized small ellipsoidal male gametophytes of *D. tenuissima*, culturing protoplasts in PES medium at 25˚C under a 14:10, light : dark condition using an incubator (NK system) [17].

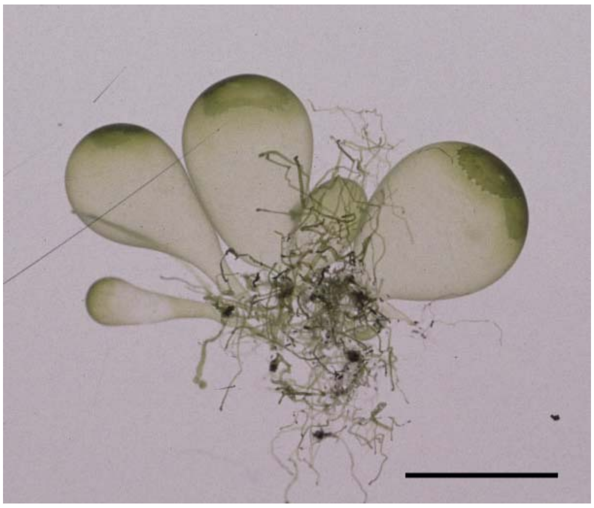

Figure 1. *Male gametophytes of Derbesia tenuissima. Both male and female gametophytes are similarly ellipsoidal in shape. Scale bar=2cm.*

Culture experiments

The grained CRDF was fixed on the bottom of cylindrical glass vessels (3 cm in radius and 8.5 cm in depth) with 50 mL of 1 % agar (Wako). Five male gametophytes of *D. tenuissima* were cultured in each vessel with 100 mL seawater at 25 ˚C under a 14:10, light : dark condition. We explored three different experimental regimes: 1) 5 g of CRDF; 2) 15 g of CRDF; 3) 1 % agar only (control). The size of each gametophyte (i.e. radii on the minor and major axes) was measured every week and the volume was calculated. At the beginning of the experiments, there was no significant difference in the mean volumes of gametophytes among the regimes. Seawater used in the culture experiments was drawn at the field study site (below) and autoclaved (121 ˚C, 20 min) before use. Chemical characters of seawater (i.e. pH and the densities of NO_3^-, NO_2^-, PO_4^{3-} and NH_4^+) after the two experiments (i.e. 15 g of CRDF and 1 % agar only) were analyzed using High Performance Liquid Chromatography (HPLC).

Field study

Our field study was carried out at our study site in the preserved area of the Marine Biosystems Research Center of Chiba University located in the Boso peninsula, Japan (35˚08'N, 140˚11'E) in 2004. Samples of seawater were weekly collected from July to December. Ammonium, Nitrate, Nitrite and Reactive phosphorus were quantitatively analyzed using HPLC. We calculated the ratios of TIN (N = Ammonium + Nitrate + Nitrite) to RP (P = Reactive phosphorus) and compared them with the Redfield ratio [13]. [The Redfield ratio refers to the molar ratio of carbon (C), nitrogen (N) and phosphorus (P) in plants estimated by using phytoplankton. When nutrients are not limiting, they have the following molar ratio of elements: C : N : P = 106 : 16 : 1. Thus N:P ratios less than 16 mean they are under nitrogen limiting conditions, and *vice versa*.]

We made a series of test plates that include the carbonaceous material (i.e. 0, 2.7, 2.9, 5.3 and 8.2 % w/w) with the 'eco-concrete' that was made from ash of waste to keep the shape in sea (*Fig. 2*). These five plates were fixed in the upper intertidal zone during a low tide using stainless bolts making a pentagon [12]. We visited them monthly and counted the numbers of individuals of each species of seaweeds growing on each plate.

Figure 2. *Plates for the field test.*

Results

Ultrastructure

In a case where the proportion of CRDF was low (3%), the surface of the sample was very smooth with few particles (*Fig. 3a*). As the proportion of CRDF increased (20%), carbonaceous grains were observed on the surface of the sample (*Fig. 3b*). In the sample with 90 % of CRDF, there were many finely uneven surface structures (*Fig. 3c*).

Figure 3. *SEM images. a) 3% CRDF; b) 20% CRDF; c) 90% CRDF.*

Water analyses

We confirmed that none of the chemical compounds listed above were eluted out from CRDF. The pH and the concentrations of ionized chemical compounds in seawater after the two of the culture experiments (i.e. with and without CRDF) are shown in the *Table 1*. Comparing the results between these two experiments, there was no critical difference in the pH and the concentrations of ionized chemical compounds except for NO_3^-. In both experiments, data on pH indicate seawater was weakly alkaline. The concentrations of NO_2^-, PO_4^{3-} and NH_4^+ were remarkably low. Only the concentration of

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NO_3^- was, however, notably increased in the experiment with CRDF. The ratios of TIN to RP of seawater at our field study site from July to December are shown in the *Table 2*. All of them were lower than the Redfield ratio.

Table 1. *Water analysis in the culture experiments.*

	pH	NO_3^- (mg L^{-1})	NO_2^- (mg L^{-1})	PO_4^{3-} (mg L^{-1})	NH_4^+ (mg L^{-1})
Experimental	8.33	23	<0.1	<0.1	<10
Control	8.77	<0.1	<0.1	<0.1	<10

Table 2. *The ratios of TIN (=Ammonium + Nitrate + Nitrite) to RP (=Reactive phosphorus) of seawater at our field study site from July to December.*

Month	July	August	September	October	November	December
TIN:RP	6	7.3	9.9	11.2	8.2	5.2

Gametophyte growth rate

The mean volumes of gametophytes of each experimental regime were plotted (*Fig. 4*). In the experiment with 5 g of CRDF, the growth rate was constantly low. The difference between the experiment and the control (i.e. agar only) was not clear. In contrast, in the experiment with 15 g of CRDF, the gametophyte growth rate was remarkably higher than the other two experiments, accelerating from the 2nd to 3rd week, and then decelerating and leveling-off after the 5th week. The mean volume of gametophytes was approximately three times larger than that of the control at the beginning of 6th week.

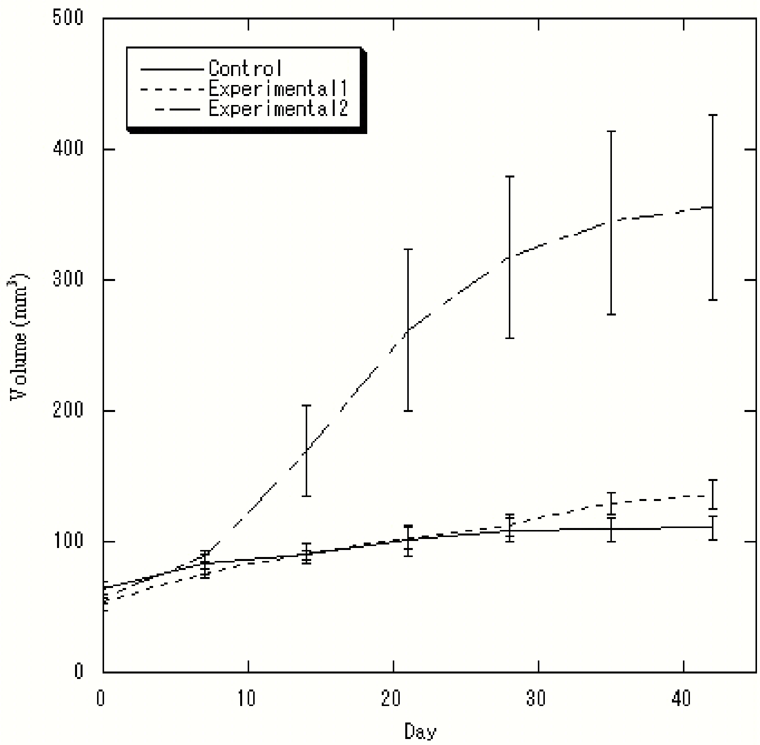

Figure 4. *The growth rates of male gametophytes of D. tenuissima with and without CRDF. Experimental 1: with 5 g of CRDF; Experimental 2: with 15 g of CRDF; Control: 1% agar only. Mean±SD (n=5).*

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Field tests

The numbers of macroalgae that were growing on the surface of the test plates after two months are shown in the *Fig. 5*. The results of the field tests might be appropriately shown by these numbers as a whole because only one species of a green alga, *Ulva conglobata* Kjellman, migrated on the plates by the end of this study and their size was still too small to compare their size. *Ulva* is an isomorphic alga. So we identified individuals, but, did not distinguish gametophytes and sporophytes. A large number of *U. conglobata* plants (85 individuals) were observed on the plate with 8.20 % of CRDF. Their numbers decreased as the percentage of CRDF. We found no *U. conglobata* plant on the plate that did not include CRDF at the end of this study. We tested another series of plates which were different in shape and located in a different place within the same study site. The results were similar to those here (data not shown).

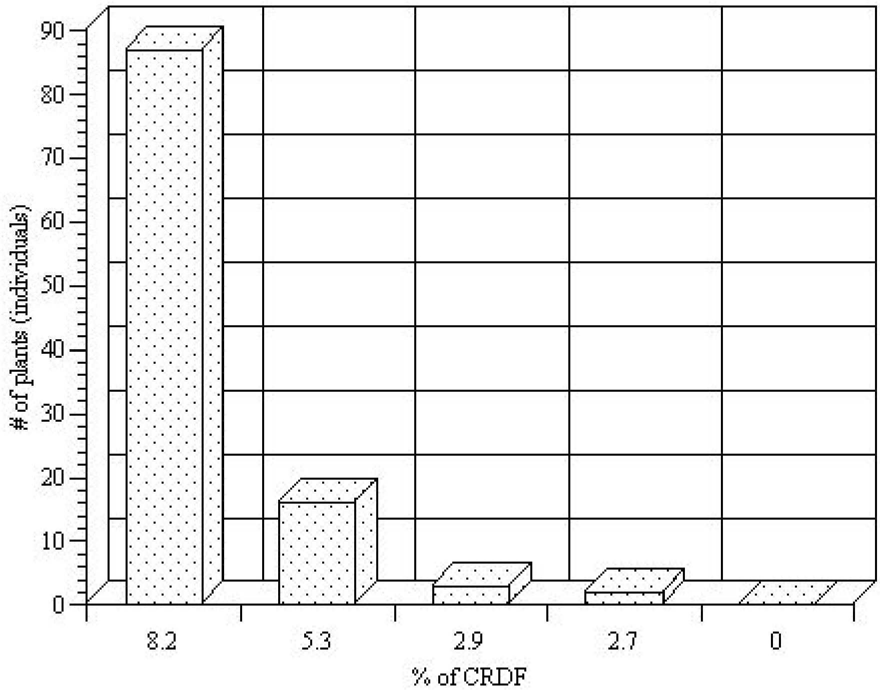

Figure 5. *The numbers of Ulva conglobata plants migrated on the test plates (Fig. 2) after 2 months.*

Discussion

Our culture experiments suggest that some substances eluted from CRDF are effective to accelerate the growth rate of algae (*Fig. 4*). The effects of dissolving substances seem to continue at least for several weeks. During the culture experiments, we have scarcely observed sexual reproduction. Therefore, most of the energy that *Derbesia* plants have might be spent for the growth. The growth was, however, inhibited by excess amounts of CRDF (e.g. 100 g per vessel in our experimental method) (data not shown). Thus, there might be the most suitable condition for growth of algae with this material.

In general, shallow-seawater habitats have relatively low N:P ratios [1]. Therefore, nitrogen is the element that most frequently limits algal growth in the sea [8]. Our analyses of seawater at our field study site confirm nitrogen is limited (*Table 2*). Meanwhile, our analyses of seawater after the culture experiments suggest that CRDF might supply nitrogen short as the form of nitrate (*Table 1*). Thus, in our culture experiments, the growth of *Derbesia* plants might be accelerated by such nitrogen. It has been suggested that nitrogen supply will be also an important constraint on global responses of terrestrial plants to elevated CO_2 [9, 14]. Another possible reason is that the quality of seawater is improved by the carbonaceous material that works as an absorbent. However, it might be less likely because there are few factors that cause serious water pollution near our field site (seawater is usually very clear). The surface structures of CRDF can not be considered here because the material was completely covered with agar. Additionally, we should note that the pH of seawater is not dramatically changed by CRDF (*Table 1*). It would be important for many aquatic organisms including algae (see [18]). The pH of seawater after the culture experiments appear to be slightly higher than the average pH of seawater (i.e. 7.7 ranging from 7.2 to 8.2). This might be caused through the rapid abstraction of CO_2 from seawater during photosynthesis of algae (see [1]).

Also, our field tests suggest that CRDF is useful to introduce seaweeds in the field, and that there may be the most suitable combination of CRDF and other materials for seaweeds to migrate on the plates, because, as the percentage of CRDF was increased, the number of migrated plants was increased (*Fig. 5*). In this study, we adduce the following three major reasons for these results. 1) Some of chemical compounds eluted from CRDF may be effective for seaweeds to grow on the plates as shown in the culture experiments. 2) CRDF may improve the quality of seawater as good adsorbent. 3) Because the surface of CRDF is rich in ultrastructural pores (*Fig. 3*) it may have a good affinity for zoospores of seaweeds as shown in activated carbon for marine microorganisms [2].

We have observed only *Ulva conglobata* plants on the test plates during our field experiment. It may be because they can flourish at the early stage of the secondary succession as a pioneer species. Actually, some other species were found on the plates after this study (e.g. *Colpomenia bullosa* (Saunders) Yamada). At our field study site, *Sargassum fusiformis* (Harvey) Sethchell, which is an economically important perennial brown alga as a good food material in eastern Asia (e.g. Japan and Korea), is one of the major dominant species. We try to introduce such species with future long-term endurance tests. There are many other reports on methods to restore seaweed forests so far (e.g. [11]). The most important merit of our study is that we use municipal solid waste (MSW) as the main ingradient. This is useful not only to reduce the costs, but also to solve two important environmental problems: atmospheric CO_2 and biodiversity. In this sense, our approach is a new type of win-win (reconciliation) ecology in marine ecosystems [15].

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