Experimental study on COD$_{Mn}$ control by using a sustainable seawater purification system built in piles and quays

Abstract
When the eutrophication in a closed sea area is progressed by the increase in inflow and accumulated pollution loads the proliferation of algae occurs and it causes seawater pollution. On the other hand, in Japan it has been seen the poor oxygen seawater or the anoxic seawater near the bottom of the sea in closed sea areas. It is necessary to maintain that the seawater is clean and rich in nature for the sustainable development. One of methods to clean the seawater in a closed sea area is the seawater purification system from the depth to the shallows built in piles and quays using purifying functions of microorganisms and the tidal energy. This system is economical and ecological because of using and combining the tidal energy and the purifying functions of microorganisms. Since the COD$_{Mn}$ of the collecting seawater from the nearshore is 2 the initial COD$_{Mn}$ is almost 8 by putting sugar adequately in seawater and mixing in order to prove the reduction of COD$_{Mn}$ by using this system distinctly. The changing process of COD$_{Mn}$ is checked by measuring COD$_{Mn}$ according to Japanese Industrial Standards (JIS K 0102). It is shown in this paper this system can be utilized in order to decrease Chemical Oxygen Demand (COD$_{Mn}$).

Keywords: sustainable seawater purification system, contact oxidation method, tidal energy, quay, seawater quality, purifying functions of microorganisms, closed sea area

Introduction
During the living action of microorganisms the material cycles such as P cycle, N cycle and O cycle are acted in the natural world. These cycles are acted during multiplication and death of organisms. When the water becomes excessively enriched with nutrients the eutrophication generates and this causes organic pollution. Water purification is the process of removing undesirable chemicals, materials and biological contaminants from contaminated water. Many techniques for the water purification were developed and published up to the present. It is shown in the reports of technique to purify the seawater by using microorganisms live in the natural world. This sustainable system described in this paper can work for a long time as long as the tide goes. It is well known we need the sustainable technique to purify the seawater for the sustainable development without delay. This sustainable technique needs to cost less and to be without environmental pollution. The seawater purification system shown in this paper built in quays and piles possesses both advantages, to cost less and to be natural as microorganisms live in the natural world. This sustainable system described in this paper can work for a long time as long as the tide can continue, that is, indefinitely in future. And this research shows this system is available for the seawater purification experimentally. This is the novelty of this research.

Sustainable seawater purification system from the depth to the shallows built in quays and piles

As one of those systems, the seawater purification system built in quays is shown in Figure 1 and another system built in piles in Figure 2. These systems have two gates, the upper gate and the lower gate and there is the gravel layer in the additionally constructed inner region (Figure 1) (Figure 2). As indicated above the eutrophication is being progressed day by day in closed sea areas in the world. Nowadays in closed sea areas in Japan it is hard to control the seawater quality in deep areas because of the poor oxygen seawater or the anoxic seawater.

Red Sea, Pollution in the bay is localized (eutrophication) in Bay of Bengal, Water pollution (BOD, eutrophication) in South China Sea.

The method in this paper uses the function of microorganisms such as decomposing organic matters. And the renewable energy, the tidal energy is used at the same time in order to move the seawater. Therefore, this system combining the function of microorganisms to purify the seawater and the tidal energy can be called as “economical” because of using the tidal energy and being cost less and as “ecological and natural” because of using the ecological function of microorganisms. This is the reason why this system is called “sustainable system”. As it is well known we need the sustainable technique to purify the seawater for the sustainable development without delay. This sustainable technique needs to cost less and to be without environmental pollution. The seawater purification system shown in this paper built in quays and piles possesses both advantages, to cost less and to be natural as microorganisms live in the natural world. This sustainable system described in this paper can work for a long time as long as the tide can continue, that is, indefinitely in future. And this research shows this system is available for the seawater purification experimentally. This is the novelty of this research.
It is necessary to maintain that the seawater is clean and rich in nature for the sustainable development. One of methods is this sustainable seawater purification system from the depth to the shallows built in piles and quays using the purifying functions of microorganisms and the tidal energy.\textsuperscript{21-23}

It is shown that this system can decrease Chemical Oxygen Demand (COD\textsubscript{Mn}) in the seawater experimentally and can be utilized in order to purify the seawater from the depth to the shallows widely using this system built in quays and partially using this system built in piles) (Figure 2).\textsuperscript{23}

![Sketch of a sustainable seawater purification system in quays](image1)

**Figure 1** Sustainable seawater purification system built in quays.

![Side view](image2)

**Figure 2** Purification process and tidal current.

The advantages of this system are\textsuperscript{21-23}

a. Using the tidal energy is called as “ecosystem”.

b. Using the purifying functions of microorganisms, decomposing organic materials is called as “ecological and natural without chemicals”.

c. Capable of purifying the seawater in the shallow area, especially also in the deep areas is called as “useful”.

d. This system built in quays or piles is simple. It is easier to construct this system additionally than to construct newly. This is called as “economical”.

This system can change the flow direction. One is the downward purification system the other is the upward purification system as shown in (Figure 3) (Figure 4). These two different flow direction systems can control the seawater quality from the depth to the shallows.

The disadvantage of this system is

i. Shells or marine plants disturb the gate to close.

A device or an idea on the bottom surface of ships and boats will be able to solve this problem. DO profiles can be introduced as Figure 5 (A), (B), (C) and (D) below. In the case of (C) in the upper mixed layer of the water column, the DO content is almost homogeneous. Generally, DO content in water bodies depend on the depth of thermocline. Typically, in eutrophic waters, a sharp decrease in DO content occurs at the depth of thermocline.
Figure 3 Sustainable seawater purification system built in piles.

Figure 4 Upward purification and downward purification.

Figure 5 DO profiles versus depth.

DO profile can be supposed to increase from the bottom to the thermocline and 0 at the bottom. The important point is that gravels are placed at the position where DO is as sufficiently large as microorganisms can decompose organic matters. From the bottom (DO=0) to the upper layer (DO>0) the seawater rises with mixing and DO increases. Therefore, DO is becoming large at the position of gravels for microorganisms to live or act and to decompose the organic matters.

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In the case of the upward purification the poor oxygen seawater flows in through the lower gate and in the inner part of the additionally constructed quays or piles and the poor oxygen seawater is rising toward the gravel layer. Because the gravel layer is located in the sufficient oxygen seawater microorganisms can live and decompose the organic compounds. Purified seawater can rise to the upper gate and flow out towards the outer sea area. Since the tidal current flows outside the closed sea areas the purified seawater can be moved out of closed sea areas towards outer areas. At the same time the seawater enters into the closed sea areas from outer areas. As all the purified seawater cannot be moved to outer areas at once some purified seawater moves to other areas in the closed sea areas by the tidal residual motion. This process can continue as long as the tide continues. Since this process continues for a long time the seawater in the closed sea areas is purified little by little sustainably.

The similar process can be applied to the case of the permeable breakwater using piles in the ocean or in the closed sea areas (Figure 3). Figure 3 shows the sustainable seawater purification system built in piles. The gravel layer is placed in a pile and there are two gates. By exchanging the gate place outside or inside a pile the seawater flows can be changed upwards or downwards (Figure 3). The seawater around a pile can be purified partially by this system.

Experimental approach

The purifying function of microorganisms is mainly affected by the seawater temperature T°C, the dissolved oxygen (DO), the sunlight energy, pH, the salinity concentration. When the constructing project of this system is planned in some area the tidal range is given as a field condition. This condition decides the discharge flow per a day as described below. Microorganisms form the biofilm on the wall and the bottom and the surface of gravels. The area S of the biofilm which is consisting of the contributing microorganisms to purify the seawater is also an important factor because the discharge of the purified seawater Q is proportional to S. In this experimental study by changing S, thickness of the gravel layer 2~8cm the effect on the ability to decompose the organic compounds is investigated by measuring COD\textsubscript{Mn}.

Experimental setup

Figure 6 & Figure 7 show the experimental setup. The central wall divides the small wave tank into two parts. The float is in the right part and the gravel layer is in the left part. This gravel layer consists of the gravels of the mean diameter of 20mm and thickness of this layer is 2~8cm. The gravels used are sieved to remain in the sieve of 19.1 mm and to pass through the sieve of 25.4mm. The shape of gravels is not a perfect sphere. And these gravels are called as the gravels of the mean diameter of 20mm.

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**Figure 6** Upward purification (in case of the float moving downwards).

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The float in the right side is going down when the stepping motor works as the rope is wound up then the seawater level is higher than the left side. Therefore, the flow occurs in the wave tank at high tide like in Figure 6, from right side to left. The seawater in the left side is going up through the gravel layer. When the water pass through this gravel layer the microorganisms purify the seawater and COD\textsubscript{Mn} is becoming smaller. At low tide the seawater flows in opposite direction. The experiments have been performed using two kinds of gravels, dry gravels in the air and wet gravels put in nearshore for a month before the beginning of the experiment and using the collecting seawater carried from nearshore.

Upward and downward purifications

In case of the upwards purification the seawater comes and flows in to the inner part of quays or piles from the lower gate and moves through gravels and next moves out from the upper gate to the outer part of quays or piles (Figure 4) (Figure 6). In case of the downward purification the seawater comes and moves through the upper gate and moves through gravels and next moves out from the lower gate to the outer part of quays or piles (Figure 4) (Figure 7). It is investigated that in two cases of upward purification and downward purification this system can reduce COD\textsubscript{Mn} in the seawater.

Methodology

The wet gravels packed in a net bag are sunk in seawater in a month near our college. At the beginning of the experiment the gravels in a month in seawater are set in the tank 2cm, 4cm, 6cm, 8cm thick like Figure 6 and the seawater carried from nearshore is put 44 cm deep into the glass tank which is 45cm wide, 120cm long, 45cm tall. The tidal model experiment is performed by moving the float up and down. When the float is moving down while the motor is winding the rope down the water surface is going up. The tidal range, the difference of the water depth is 4 cm in this experiment. Tidal difference in some coastal area is 1m then the model scale is 1/250. In Japan the tidal period is 12 or 24 hours. The experimental period is selected as 24 hours. The experiment is repeated for two weeks. The original value of COD\textsubscript{Mn} of the collecting seawater is about 2. In order to magnify the reduction process of COD\textsubscript{Mn} value from 2 to 1 the initial COD\textsubscript{Mn} is almost 8 [mg/l] at the beginning of the experiment by putting sugar adequately in the seawater and mixing. Used sugar is raw sugar which is made of plants, sugar cane and sugar beet. This used sugar is produced by Mitsui Sugar Co., Ltd. in Japan. This used sugar is not an artificial sweetener.

During the experiment COD\textsubscript{Mn}, DO (Dissolved Oxygen), the seawater temperature T [°C] and the turbidity are measured. DO and T are measured by using DO meter (HORIBA OM-51, measurable 0-19.9mg/l, made in Japan). COD\textsubscript{Mn} is measured by using Erlenmeyer flasks, magnetic stirrers, burettes, water bath machine according to JIS K 0102. The ability of purification is affected by T, DO, pH, the salt concentration. The discharge Q is supposed to be proportional to the area of the biofilm S. The discharge of the purified seawater Q is a function of these parameters and the size of quay, B and L, and the tidal range z. It is assumed that Q is expressed as the next equation:

\[ Q = v \times A = V \quad [m^3/day] = \varphi(T, DO, weather, pH, salinity concentration, S, d, B, L, z \ldots) \quad (1) \]

where \( v \) is the apparent mean velocity of the seawater in gravels, \( A = B \times L \) is the inner cross-sectional area of the additionally constructed quay portion, \( V \) is the moving volume of the seawater a day per a set of gates, the upper gate and the lower gate and \( S \) is a specific surface area and \( d \) is a mean diameter of gravels. As the tide is repeating day by day the time “a day” is selected.
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Experimental procedure

The experimental procedure is shown below briefly. Experiments are performed as follows. The study site is 2m deep, the average temperature is 20-30°C in summer and 0-15°C in winter, there is a rainy season in June in Japan. Collecting seawater site is near our college in Akashi City in Japan.

Sampling and preservation: Collecting the seawater, the volume of 300L for a vessel, at the sea shore near our college. Materials required are Erlenmeyer flasks, stirrers, burettes, constant temperature water bath, dilute sulfuric acid, silver nitrate solution, potassium permanganate solution, sodium oxalate solution.

Procedure: At first we measure original COD$_{Mn}$ value of collected seawater. Next we put the seawater into the vessels and turn on the motors and aeration machines. Then the motor works and next the float is rising and falling, that is, the seawater level is rising and falling. After putting raw sugar in the seawater and mixing initial COD$_{Mn}$, we perform experiments according to JIS K 010224). At the same time DO and T are measured.

Results and discussion

There is the Environmental Quality Standards in Japan relating to water pollution on the website). This website shows The Basic Environment Law establishes two kinds of Environmental Quality Standards relating to water pollution, environmental water quality standards for protecting human health and environmental water quality standards for protecting the living environment. The latter standards in coastal waters show standard values in pH, COD$_{Mn}$, DO, Total coli form etc. below. COD$_{Mn}$ needs to be less than or equal to 2 [mg/L] for A class (for Fisheries primary and for Swimming etc.), 3 [mg/L] for B class (for Fisheries secondary and for Industrial water etc.), 8 [mg/L] for C class specified by Environmental Water Quality Standards Concerning the Conservation of the Living Environment, Environmental Quality Standards, the Basic Environment Law in Japan. In this paper the purpose is to improve the level of COD$_{Mn}$ concerning the conservation of the living environment.

The usefulness of this purification system is described by showing the difference between the case using the wet gravels with microorganisms and without gravels, the difference between using the wet gravels and the dry gravels and the difference of COD$_{Mn}$ change with time between different thicknesses of the gravel layer experimentally.

Discharge Q of the seawater

The volume V of the seawater is exchanged for a day from the inner part to the outer part of quays or from the outer part to the inner part. V is expressed as

$$V = BLz$$  \hspace{1cm} (2)

Where B is the width of the additionally constructed quay and L is the length of the quay per one set of gates, the upper gate and the lower gate (Figure 1) and z is the tidal range. The discharge Q is expressed as

$$Q = V \frac{m^3/day}{BLz}$$  \hspace{1cm} (3)

Where v is the apparent mean velocity of the seawater in gravels. On the other hand, the discharge Q through the gate

$$Q = v_A \times A_1$$  \hspace{1cm} (4)

Where $v_A$ is the mean seawater velocity through the gate, D is the diameter of the circular gate and $A_1$ is the area of the circular gate.

The following nondimensional parameter P can be introduced. P is defined as the ratio of (Q/L) to (SvD).

$$P = \frac{Q}{L} \times (S \times vD)$$  \hspace{1cm} (5)

S is a biofilm area (see 5.2) and a function of the thickness t of the gravel layer and the diameter d of gravels. Smaller is the size of gravels the wider is the specific area of gravels. The efficiency of purification becomes greater proportionally to S. The greater S is considered to be desirable. But when d is too small the permeability can appear considerably and it cannot flow easily because of the frictional energy loss. The thickness t of the gravel layer should be greater than the tidal range z since microorganisms should face the seawater longer to decompose the organic compounds.

$$t \geq z$$  \hspace{1cm} (7)

t can be supposed to be equal to z.

The ratio of the discharge Qp in prototype to the discharge Qm in model can be calculated according to Froude similarity. From the point of view of microbiology the apparent velocity v must be smaller than the critical velocity, for example in case of the slow filtration, 3m/day.

Biofilm area S

When the seawater is put into the wave tank microorganisms living in the seawater make the biofilm on the surfaces of the wave tank, on the center wall and on the surface of gravels. Microorganisms on the surface of the biofilm and in the seawater can decompose the organic compounds. There are the biofilm area $S_b$ on the surface of gravels, the specific surface area and the biofilm area $S_w$ on the wall, $S_t$ on the bottom of the tank in case of model experiments and the biofilm area $S_{b1}$ on the wall and the bottom of the quay in case of the prototype. Table 1 shows the list of biofilms $S_b$ on the gravels, $S_w$ on the wall and $S_{b1}$ on the bottom in experimental cases.

When gravels are supposed to be cubic the specific surface area $S_1$ is approximately expressed as

$$S_1 = \frac{6V}{d}$$  \hspace{1cm} (8)

$$S_1 = \frac{\pi V}{d}$$  \hspace{1cm} (9)

Where d is the mean diameter of gravels and $V_b$ is the volume of gravels, $V_a$ is the apparent volume of gravels including voids, $V_a = BLt$. Sw in experiments is $2(hL+Bh)$, $S_b$ is BL and $S_{b1}$ is $2hL$ in case of the prototype where h is the water depth.

Using wet gravels with microorganisms and without gravels

Figure 8 shows the results of values of COD$_{Mn}$, DO and T changes with time during experiments and the difference between the cases using wet gravels and without gravels. At the beginning of the experiment

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the initial COD_{Mn} is almost 7 by putting sugar adequately in seawater and mixing. This shows that without gravels microorganisms in the seawater can also decompose the organic compounds and COD_{Mn} can be decreased for a short time and that COD_{Mn} using wet gravels with microorganisms is smaller than that without gravels. Microorganisms living in the seawater can decompose the organic compounds. This shows that this system using contact oxidation method can reduce COD_{Mn}. Biofilm area in case of wet gravels is greater than that in case of without gravels. Therefore, COD_{Mn} in case of wet gravels decreases greater than that in case of without gravels.

Table 1 shows the list of biofilm areas in experiments. The water depth h is 40cm. As it can be seen from Table 1 S_1 is relatively smaller than S_2 in case of t=2cm and 4cm.

Table 1 Biofilm areas and specific surface area of gravels supposed to be sphere in experiments (h=40cm)(t: thickness of a gravel layer)

| Biofilm area [cm^2]                        | t=2cm | t=4cm | t=6cm | t=8cm |
|-------------------------------------------|-------|-------|-------|-------|
| Specific surface area S_1, approximately [1/cm] | 8407  | 18246 | 2522  | 36492 |
| Apparent volume V_a [cm^3]                | 5355  | 10710 | 16065 | 21420 |
| S_{w1} (Biofilm area on the wall in the gravel layer side) [cm^2] | 8360  | 8360  | 8360  | 8360  |
| S_{b1} (Biofilm area on the bottom in the gravel layer side) [cm^2] | 2678  | 2678  | 2678  | 2678  |
| S_{w2} (Biofilm area on the wall in the opposite side of the gravel layer) [cm^2] | 8360  | 8360  | 8360  | 8360  |
| S_{b2} (Biofilm area on the bottom in the opposite side of the gravel layer) [cm^2] | 2678  | 2678  | 2678  | 2678  |
| S=S_1+S_{w1}+S_{b1}+S_{w2}+S_{b2} [cm^2] | 30483 | 38891 | 47298 | 55705 |

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Using wet gravels and dry gravels

Figure 9 shows the results of values of COD$_{mn}$, DO and T changes with time during experiments and the difference between the cases using wet gravels with microorganisms put in the seashore for a month and dry gravels. At the beginning the initial COD$_{mn}$ is almost 8 by putting sugar adequately in seawater and in the mixing. This shows that COD$_{mn}$ changes with time are almost same and that it does not need the gravels put in the seashore for a month. The biofilm of microorganisms may be formed for a short time relatively. The biofilm area in this experiment may be on the wall surface of the tank and on the surface of gravels. The biofilm area is calculated and shown as Table 1. For a short time after putting the seawater in the tank the biofilm may be formed on the surface of gravels and the wall. Nondimensional parameters P are becoming smaller as the thickness of the gravel layer becomes greater in Table 1.

Specific surface area in case of wet gravels is same as that in case of dry gravels. Therefore COD$_{mn}$ decreases almost same in two cases (Figure 9).

Relation between COD$_{mn}$ change and the different thicknesses of the gravel layer

Figure 10 and Figure 11 show the results of values of COD$_{mn}$, DO and T changes with time during experiments. At the beginning of the experiment the initial COD$_{mn}$ is almost 8 by putting sugar adequately in seawater and mixing. Figure 10 shows the case of the thickness of gravel layer t is 2 cm and Figure 9 shows the case of t=8cm.
DO is almost 8~10 in two cases and T is 9~13°C in case of t=2cm and 9~16°C in case of t=8cm. Obviously COD$_{Mn}$ is becoming smaller. It shows that this system can reduce COD$_{Mn}$ in seawater.

It is shown that in case of t=8cm COD$_{Mn}$ decrease more rapidly than in case of t=2cm. It shows that the greater is the area of the biofilm S the greater is the effectiveness to reduce COD$_{Mn}$ during the initial same time. Table 1 shows that S in case of t=8cm is greater than S in case of t=2cm. As this is mentioned above S should be greater to reduce COD$_{Mn}$ on the condition that the flow velocity in gravels is enough small for microorganisms to decompose the organic compounds. The period of the tide is 24 hours and the tidal range z is 4cm in this experiment. Averaged seawater velocity is about 4cm/12 hours=0.001mm/sec. It is sufficiently slower than the velocity in case of the slow filtration, 3m/day=0.035mm/sec.

Application to the field

When the field to construct this purification system is given the tidal range z, the width of quay B, the length per the gates L is also given. According to eq. (3) Q is calculated. t is supposed to be equal to z. When the diameter of gravels D is given S is calculated by using eq. (8) or (9). Apparent mean velocity v in gravels is calculated by using eq. (4). v can be checked as slow as microorganisms can decompose the organic compounds and S can be checked as wide as the seawater volume can be purified. The nondimensional parameter P is calculated using eq. (6).

This system built in piles is suitable for relatively small areas around the piles and the system built in quays is suitable for wide areas along and in front of the quays. This system needs the tidal motion and the tidal current to carry the purified seawater to another place. As the tide continues day by day and year by year it can maintain the seawater clean.

Conclusions

The following conclusions are drawn from this study:

I. The initial COD$_{Mn}$ is almost 8 by putting sugar adequately in seawater and mixing. This method can be utilized to measure COD$_{Mn}$ change with time effectively. By applying this method it is shown that this system can decrease Chemical Oxygen Demand (COD$_{Mn}$) in the seawater experimentally and can be utilized in order to purify the seawater from the depth to the shallows widely using this system built in quays and partially using this system built in piles. The COD$_{Mn}$ control to decrease COD$_{Mn}$ in the seawater continuously step by step is able to continue as long as microorganisms are living and active and the tidal motion continues. As a result of the fact above the improvement effect of the seawater quality will appear obviously.

II. COD$_{Mn}$ change with time between the two cases, using wet gravels and dry gravels, is almost same therefore it is not necessary to put gravels in the seawater for a month in order to acquire microorganisms on the surface of gravels before the beginning of the experiments.

III. The greater is the biofilm area the greater is the effect of reducing COD$_{Mn}$.

This system can be utilized to maintain the seawater is clean. This system using the tidal energy and purifying functions of microorganisms is useful for sustainable development.

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None.

Conflict of interests

Author declares that there is no conflict of interest.
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