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Characterization of Humic Substances in Sediment on Joumine Reservoir in Tunisia

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Abstract: In arid and semi-arid land, the rehabilitation of reservoirs such as sediment dredging is necessary in order to utilize the water resource sustainably, but it has not been carried out due to its high cost of operation in developing countries. Thus, valorization of the sediment to generate income which will be used to cover the cost of operation is discussed. In this study, the content and characteristics of humic substances in the sediment were examined as a first step toward the utilization of the sediment as a material for soil amelioration. Humic acid and fulvic acid (JS-FA) in the sediment of Joumine reservoir located in the northern part of Tunisia were extracted according to the standard method of International Humic Substance Society. The volume of the extracted material as humic acid was so small that it was not possible to detect. On the other hand, the content of extracted fulvic acid was approximately 0.5% of the organic matter content of the sediment. Then, in order to confirm whether the extracted material is fulvic acid or not, the absorption spectrum was determined by measuring FT-IR spectroscopy and was compared with the spectra of fulvic acids of peat (CP-FA) and weathered coal (WC-FA). Results show that the spectrum of JS-FA was similar to the spectra of CP-FA and WC-FA, confirming that JS-FA was fulvic acid. Additionally, the FAs extracted from the sediment collected in August and December 2010 had different characteristics compared to the FA from the sediment in the Japanese reservoir.

Key Words: FTIR, Fulvic acid, Reservoir, Sediment, Semi-arid land

1. Introduction

Tunisia, one of the North African countries, is an area where there is a big environmental gradient because the distance from its north which has a Mediterranean climate to the south area with an arid climate is 400 km long. In this region, a great variety of living species can be found. It has been reported that some plants exposure to produce useful compounds caused by environmental stresses such as solar radiations, temperature, saline-alkali soil and the others. Some of the olives, aromatic, medicinal plants, and halophytes have already been cultivated as commercial products. Considering sustainable utilization of bio-resource, water resource management is one of the essential points in the region.

Generally, agriculture in arid and semi-arid regions is dependent on groundwater for irrigation or water resources. In Tunisia, however, water transfer systems consist of pipe lines and canals constructed to transfer surface water from the mountain area in the north to the coastal urban area and farming area where the demand for water is high. Thus, the ratio of water supply from surface water and groundwater is 50/50 in this country (Irie *et al.*, 2009)

Currently, the population in Tunisia is increasing, so it is assumed that in addition to the agricultural water scarcity, the daily life water supply is also getting scarce. However 97% of available surface water in Tunisia has already been used or planned to exploit. It is so difficult to exploit new resource of surface water as it is also necessary that the present reservoirs will be operated sustainably.

In general, the storage capacity of reservoir is decreasing year by year because of sedimentation. Many reservoirs in Tunisia have the same problem (Ben Mammou and Laouti, 2007), so the rehabilitation of these reservoirs by for example, dredging operation is necessary. However, the North African countries, including Tunisia, cannot perform the reservoirs rehabilitation because of financial difficulties. As a measure to be taken, it is suggested that the cost associated with the operation will be covered by the proceeds from valorizing and utilizing the sediment in reservoirs.

This research, from this view point, focused its attention on humic substances (HS) in the sediment. Fulvic acid (FA), which is one of the HS, is approved as a food product, and its anti-allergy property has also already been reported (Yamada *et al.*, 2007). It was also reported that HS renders persistent organic chloride harmless and ameliorates saline-alkali soil which is a problem in arid and semi-arid land (Fukushima, 2007).

On the other hand, as part of the research on HS in sediment on reservoir, Toyoda *et al.* (2009) reported on the utilization of HS from reservoir in Japan. However, the number of research on HS in the reservoir is not more than the

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research devoted on freshwater lake and brackish lagoon.

It is thought that HS originates from the organic matter supplied by plant debris from the upstream basin (external source) and phytoplankton in reservoir (internal source). The characteristics are different because of the differences in climate, natural circumstances and social surroundings. However there is no previous research on HS in sediment of reservoir in semi-arid and arid land.

This paper investigated the characteristics of HS as a first step to utilize the sediment from water reservoir in semi-arid and arid lands with the objective for an efficient water management and utilization of bio-resource.

2. Materials and methods

2.1. Study site

In this paper, humic substances from sediment of Joumine reservoir, located in the north of Tunisia, were extracted and analyzed. The upstream watershed area of Joumine reservoir is 418 km^2 and the reservoir capacity is 130 million m^3 which ranks 5th in water storage capacity among all the water reservoirs in Tunisia.

Salinity of the water in the reservoir is lower than the other reservoirs in Tunisia that the water in the Joumine is utilized not only for drinking and irrigation but also to dilute the water from other reservoirs which contain relatively higher salinity.

This reservoir has been in use since 1986. The mean residence time is about 2 years. It is longer than the residence time of reservoirs in Japan, which is at most 1 year or less. Also water current in the reservoir is low so that the sediment easily accumulates in the bottom.

2.2. Sample collection

In August and December 2010, sediments were collected from the bed of the central part of the reservoir by using an Ekman-Birge bottom sampler (RIGO CO., LTD.). Collection point is shown in **Figure 1**. The collected sample was packed into plastic bags in the field, then brought to Japan by air and kept in 4°C prior to analyses.

The depth of sampling location is about 25 meters. Vertical profiles of the water quality has been measured in August and December 2010 and it was confirmed that the water in the points where the depth is more than 10 meters, the concentration of dissolved oxygen is low and this is caused by thermal stratification in summer (Irie *et al.*, 2011). In addition, it was reported that the low oxygen concentration occurs for 6 months, from April to October.

2.3. Physicochemical parameters

In the laboratory, after the sediment sample was dried in an

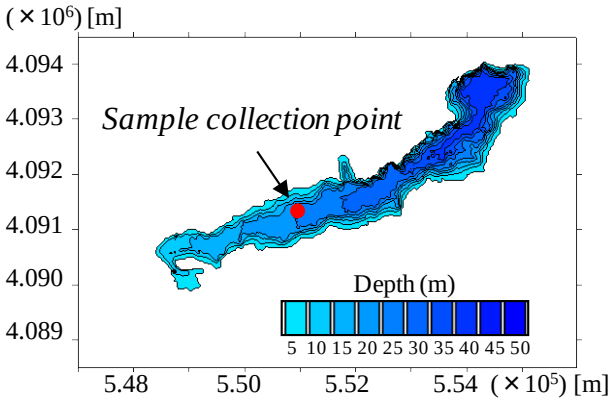

Fig. 1. Location of sediment sample collection on Joumine reservoir.

Table 1. General characteristics of the sediment collected in Dec. 2010.

pH (H_2O)	8.6
EC (H_2O)	0.444 mS/cm
moisture	59.4 %, as received
IL (1 h at 750 °C)	18.4 dry%

oven at 60°C for 48 h, the pH (1:2.5, H_2O) and electric conductivity (EC; 1:5, H_2O) were measured by Multi-Parameter PCTestr 35 (OAKTON Instruments). Moisture and ignition loss (IL) were determined by the following procedure: The weighed sample of sediment was placed in dry and weighed porcelain crucible, the crucible and its content were dried in an oven at 105°C for 24 h. After being allowed to cool in a desiccator, the crucible was reweighed. The percentage of moisture was calculated using equation 1:

$$\text{Moisture}\,[\%] = (w_0 - w_{105}) / w_0 \times 100 \quad (1)$$

where w_0 is the initial weight of the sample and w_{105} is the weight of the sample after being heated at 105°C. Similarly, to determine the IL, weighed samples of the sediment in dry weighed crucible were placed in a muffle furnace at 750°C for 1 h. The IL was calculated using equation 2:

$$\text{IL}\,[\%] = (w_{105} - w_{750}) / w_{105} \times 100 \quad (2)$$

where w_{750} is the weight of the sample after being burned at 750°C.

2.4. Isolation of humic substances

Humic acid (HA) and fulvic acid (FA) in the sediment were extracted according to the standard method of International Humic Substance Society (IHSS).

2.5. FT-IR spectroscopy

Spectra were recorded on a Fourier-Transformed Infrared (FT-IR) spectrophotometer (JASCO Corp., FT/IR-300E, Rev. 1.00). The KBr pellets were made from 1 mg HS and 95 mg KBr. The spectra resolution was 4 cm^{-1}. A pellet consisting of only KBr was used as the reference material.

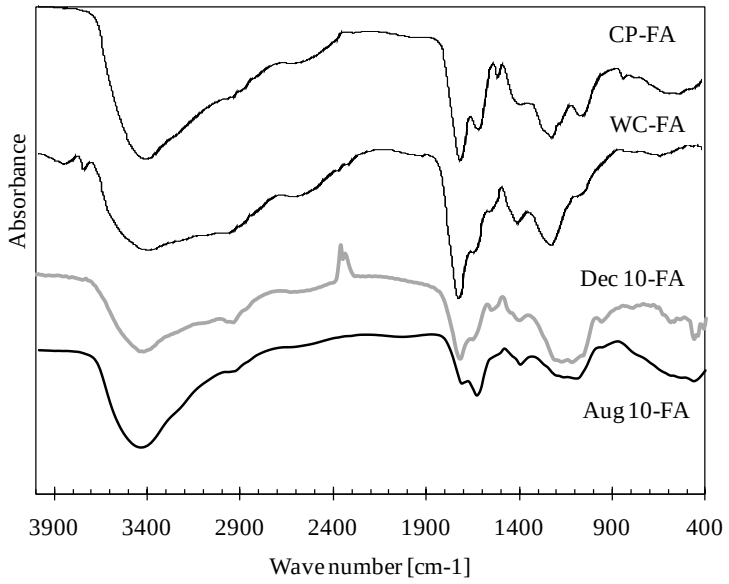

Fig. 2. FT-IR spectra.

Table. 2. Elemental compositions of fulvic acids.

Sample name: Fulvic acids (FAs)	C [%]	H [%]	N [%]	O [%]	Atomic ratios		Ash [%]	References
					H/C	O/C		
August 2010	50.1	6.0	4.9	39.1	1.44	0.59	48.4	
December 2010	52.1	5.7	4.4	37.7	1.32	0.54	26.7	
Ono Reservoir	50.7	4.2	2.5	42.7	0.98	0.63	-	Hasegawa *et al.* (2004)
Mean of the Soil	45.3	5.0	2.6	46.2	1.35	0.78	-	Rice and MacCarthy (1991)
Mean of the Marine	45.0	5.9	4.1	45.1	1.56	0.77	-	
Mean of the Peat	54.2	5.3	2.0	37.8	1.20	0.53	-	

2.6 Elemental analysis

The carbon, hydrogen, and nitrogen contents of the two FAs extracted from the sediment were determined using the Perkin-Elmer 2400 CHN Elemental Analyzer. Oxygen content was calculated for the difference of C, H, and N. Total ash was measured as the following: FA samples dried at 105°C for 24 h in dry weighed crucible was placed in a muffle furnace at 600°C for 2 h.

3. Results and Discussion

3.1. General characteristics of sediment and content of humic substances

Table 1 shows the general characteristics of sediment. As a result, we could extract FA only, its content was approximately 0.5% of IL. On the other hand, HA was determined to be present during the extraction process, but we could not obtain sufficient sample.

3.2. Comparing with another humic substances

Figure 2 shows the FT-IR spectra of the FAs (Aug 10 - FA and Dec 10 - FA) from the sediments collected in August and December 2010 and the FAs in weathered coal (WC-FA) and Canadian *Sphagnum* peat (CP-FA) (Yamada, 2002; Yamada *et al.*, 2007)

The spectra of the Aug 10- and Dec 10- FAs were generally similar to WC- and CP-FAs, proving that these extracts are fulvic acid. However there were a few differences between the Aug 10- and Dec 10-FAs. For example, the shapes of the spectra around 1700 and 1620 were different as shown in Figure 2. And also, Dec 10-FA had the peak at 1540 but Aug 10-FA do not. Although what these differences mean is not known yet, as previous described, water quality around the bed of the reservoir changes with season in summer (August) and winter (December), especially, water-dissolved oxygen refers to the process of organic matter decomposition. In other words, it is thought that the characteristics of FAs in reservoir changes due to the oxygen concentration in water which is aerobic in winter and anaerobic in summer.

The results of the elemental analysis are shown in **Table 2**. From the results, while the differences between the two sediments collected in August and December 2010 was not

significant, there was a difference in the atomic ratios between the Japanese and Tunisian reservoirs. In addition, C and O contents of the Joumine sediments are similar to Peat. Thus, it is thought that one of the reasons for the decomposition process is the aerobic and anaerobic conditions of the sediments.

4. Conclusion

It was confirmed that humic substances, especially fulvic acid, is present in the sediment of reservoir in Tunisia. The characteristics of fulvic acid in the sediment are generally similar to the ones in weathered coal and peat. There are a few different characteristics between the FAs extracted from the sediment collected in August and December 2010, and from the sediment in the Japanese reservoir. Although the real cause cannot be determined, it seemed that the water condition, especially, the aerobic and anaerobic condition in the decomposition process, is the one of the factors.

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