Production and Effective Utilization of Carbonized Sludge of Industrial Wastewater Treatment Plant

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Summary: Industrial wastewater sludge was successfully converted into a carbonized product of maximum environmental benefits. Carbonization was carried out to determine an optimum temperature conditions in order to get low temperature carbonization product of required characteristics. Stack gas emissions throughout the course of carbonization and fuel quality characteristics of the carbonized product were also monitored. Analyses of the carbonized product for its possible applications as farm land additive and as green fuel utilization were also conducted. Main objective of the study was to get comparative study of the carbonized sludge; a by-product of industrial wastewater treatment plant, with the sludge stabilized by other heat treatment techniques.

Introduction

The rate of wastewater treatment has been kept improving significantly in Korea since last decade and now has become almost equal to the developed nations. Approximately 4.2 million tons of industrial sludge is being generated each year in the country as a by-product of industrial wastewater treatment plant. Management of industrial sludge is becoming a serious concern due to increasing volume of sludge, demand for lower pollutant discharges, ban on direct landfilling and rise in disposal costs [1, 2]. Sludge management facilities have been offering many alternatives like incineration, composting, landfilling, and solidification/stabilization etc. for the safe disposal of sludge [3-5]. Conversion of sludge into a carbonized product is another newly introduced alternative of the sludge management that attracts a great deal of attention as it provides an environment friendly and economically sound solution for bio-solid disposal. In carbonization technology, sludge is being converted into carbon-containing residue through a selective technique of heat treatment. Dewatered sludge is first converted into dried cake which is then heated under air-strived environment where it is carbonized and converted into a char like product which is rich in carbon also known as carbide [6]. Carbon mono oxide, methane, ethane, and ethylene produced during the carbonization process are recovered from the system. The recovered gases are used to heat up the reactor. While only the drying process needs external fuel for keeping a certain temperature, carbonization is sustained with burning the own gases.

Research has focused on the characterization of carbonized sludge for its effective and economic utilization in order to get zero waste emission objectives. Marcos *et al.*, [7] successfully carbonized the sewage sludge by flash carbonization technique in a short time of 10–15 minutes. They also discussed the behavior of ash and heavy metal ions in the sewage sludge charcoal during flash carbonization process. Hakuei *et al.*, [8] characterized carbonized sludge having high calorific value and could be utilized as secondary fuel in electric power generation industries. Exothermic or auto-ignition characteristic of carbonized sludge was studied by Malviya *et al.*, [9]. They found that the sample that easily generates heat has less pore volume, low true density and great deal of volatile materials and such product is produced by insufficient carbonization. Their tests also showed that the carbonized product with low refining ratio has high hydrogen and carbon (H/C) ratio and active self-exothermic characteristics. The carbonized sludge is chemically stable, light in weight, easy to handle having high absorbability and heat value. Other studies have focused on the

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conversion of sewage sludge into carbonized product while in our study we successfully carbonized the sludge taken form industrial wastewater treatment plant. This study determines an optimum temperature for the production of carbonized sludge of the maximum environmental benefits. The work also offers a kind of comparison between the material produced by carbonization and the material produced by using other techniques of sludge stabilization. Effective utilizations of the carbonized material are also discussed in the paper.

Results and Discussion

Dewatered Sludge Drying

Table-1 shows drying behavior of dewatered sludge. It suggested that increase in rpm of the drum has nothing to do with the drying efficiency of the sludge; however, increase in drying period of sludge significantly increased the drying efficiency. Sludge was carbonized at three different temperatures *i.e.*, 350 °C, 450 °C and 550 °C. Sludge carbonized at 450 °C had high calorific value and fixed carbon than the sludge carbonized at a high temperature 550 °C (Table-2). Although calorific value of the carbonized sludge was relatively lower than the calorific value of dewatered and dry sludge but volume of carbonized sludge was reduced to 50 % of the volume of dry sludge that makes transportation and handling of carbonized sludge easier.

If heat value is the only concern, a dried sludge seems to be a better choice. However, dried sludge smells bad and is subject to spoiling. Carbonization is the better choice since carbonized product does not smell bad while burning and could be stored for long time without the concern of putrefaction or spoilage [10].

Table-3 indicates that as the temperature increases in carbonization, inorganic non combustible contents are going to be increased in the ultimate product than organic contents. As high temperature (550 °C) increased amount of ash contents in the carbonized product it, however, reduced amount of fixed carbon subsequently reduced its calorific value as compared to the product carbonized relatively at low temperature, *i.e.*, at 450 °C.

Heavy Metal Ions in Carbonized Sludge

Leaching tests on carbonized sludge were performed to check the amount of heavy metals in the leachate. All the heavy metal ions detected in the leachate were found below limit even in the material carbonized at low temperature (350 °C). Amount of arsenic and mercury were found below detection limit *i.e.*, .001 ppm (Table-4).

Exhaust Gas Analysis

Exhaust gases generated during combustion were passed through exhaust gas treatment tower for

Table-1: Drying analysis of wastewater sludge at 450 °C.

Sample type	Moisture contents (%) Before drying	Moisture contents (%) After drying	Drying efficiency (%)	Contact time (min)	Drum speed (rpm)	Eccentric speed (rpm)	Drying temperature (°C) Inlet	Drying temperature (°C) Outlet
1	81.3	15.6	80.85	20	3.0	167	409	153
2	81.2	10.9	86.58	30	2.0	167	413	193
3	81.2	5.5	93.23	35	1.0	167	414	210

Table-2: Heat value characteristics of various sludge types.

Sludge type		Moisture (%)	Volatile (%)	Ash (%)	Fixed Carbon (%)	Calorific value kcal/kg
Dewatered sludge		80.65	61.36	33.29	5.35	4,104
Dry sludge		11.41	60.97	32.29	6.74	4,128
	350 °C	1.26	46.62	41.45	11.99	3,195
Carbonized sludge	450 °C	1.23	45.29	41.54	13.17	3,388
	550 °C	0.22	39.36	48.99	11.65	3,048
	Mean	0.90	50.72	39.51	12.27	3,210

Table-3: Elemental analysis of carbonized sludge.

Sludge type	C (%)	H (%)	O (%)	N (%)	S (%)	Cl (%)	Ash (%)
Dry sludge	32.47	4.46	23.06	4.58	3.03	0.11	32.29
Carbonized (350 °C)	30.49	2.16	17.03	4.41	0.00	0.19	41.45
Carbonized (450 °C)	30.25	2.19	16.85	4.54	4.43	0.20	41.54
Carbonized (550 °C)	28.70	0.00	12.04	3.95	0.00	0.20	48.99

Table-4: Heavy metal ions analysis of carbonized sludge.

Sludge type	Cr^{+3} (mg/l)	Cd^{+2} (mg/l)	Pb^{+2} (mg/l)	As^{+3} (mg/l)	Hg^{+2} (mg/l)	Cu^{+2} (mg/l)	Fe^{+2} (mg/l)	Zn^{+2} (mg/l)	Ni^{+2} (mg/l)	Mn^{+2} (mg/l)
Dry sludge	0.60	ND	0.03	*ND	ND	0.03	8.60	0.44	7.44	0.93
Carbonized (350 °C)	0.08	ND	0.01	ND	ND	0.02	7.49	0.21	0.08	0.79
Carbonized (450 °C)	0.08	ND	0.02	ND	ND	0.02	5.00	0.20	0.12	0.50
Carbonized (550 °C)	0.03	ND	0.01	ND	ND	0.08	0.88	0.06	0.27	0.84

*Not Detected

the removal of soot and dust by cyclone and fabric bag filters. Gas stream contained particulate matter (PM_{10}) of the size of around 10 μm. The filter processed the exhaust gases at a rate of 10 Nm^3/min capacity having filtration area 10.5 m^2. The gas after fabric bag filter passed through wet scrubber unit that treated the gas at a rate of 12 Nm^3/min. Stack gas analysis showed that the contaminants like SO_x, NO_x, HCl, and PM_{10} were found below discharge limit of air quality standards of stack gas emissions of environmental regulatory agency (Table-5). By adopting an independent combustion furnace, the carbonized gases were combusted at an appropriate air ratio and combustion temperature enabling stable and clean combustion. The release of N_2O in carbonization process, a gas with a greenhouse effect 310 times more than that of carbon dioxide [11], can be reduced to a level far lower than the levels released by incineration generally adopted for wastewater sludge management techniques.

Table-5: Stack gas analysis at varying temperature of carbonization.

Contaminants	Units	Emission standard	Observed value 350 °C	450 °C	550 °C	Mean
Dust	mg/Nm^3	100	6.0	7.3	6.4	6.6
SO_x	ppm	100	41.4	32.6	36.1	36.1
NO_x	ppm	150	35.8	42.3	43.7	40.6
HCl	ppm	50	14.2	12.6	11.4	12.7

Weight Loss in Carbonization

Table-6 showed a comparison of weight loss of sludge during carbonization over the other conventional methods of sludge stabilization like composting, drying, incineration and fusion [12]. Highest weight reduction is achieved in case of carbonization.

During carbonization, weight of sludge is reduced to 99 %. During the carbonization process, approximately 80 % of organic substance in the sludge volatilized as gas through carbonization and the remaining substance of approximately 20 % is immobilized in the carbonized product. Oxygen and hydrogen in dehydrated sludge gasify through carbonization and approximately 70 % of the carbon which is main element in dry solid substance also gasifies but 30 % of it remained in carbonized products. The selective immobilization of carbon through carbonization is also confirmed by the fact that the carbon content of organic substance in carbonized products accounts for approximately 80 % which is higher value compared with those of dehydrated and dry cake [13].

Heat Value Analysis of Carbonized Sludge

Table-7 shows a comparison of heat contents of carbonized sludge with the heat contents of other combustible material. Carbonized material has calorific value 3210 kcal/kg which is roughly half of the coal's or equal to calorific value of low quality coal. Carbonized material, therefore, could be burned with coal at thermal power generation plant. Mixing ratio should around 1 % of coal. Additionally, through carbonization, dewatered sludge was reduced to its volume to 1/12 and its offensive odor was deprived of which enable easy handling of the product.

Table-8 compares fuel quality of dry and carbonized sludge with the Korean Technical Standards for Quality of Coal. This comparison suggested that carbonized material could alone be

Table-6: Amount of moisture contents and weight loss of different sludge stabilization products.

Parameter	Solidification	Composting	Drying	Carbonization	Incineration	Fusion
Moisture (%)	22	11	11.4	0.9	1	0.0
Weight loss (%)	47	46	85.80	98.90	95	97

Table-7: Heat contents analysis of different types of waste material and fuels.

Type	Waste Material: Food	Plastic	Paper	Textile	Timber	Leather & Rubber	Fuel: Methane	Carbonized sludge	Dry sludge	Gasoline	Light oil	Coal	Coke
Calorific value kcal/kg	3,446	8,064	4,092	4,309	4,193	5,256	13,270	3,210	4,128	11,032	10,685	8,076	6,500

Table-8: Fuel quality analysis of dry and carbonized sludge.

Parameters	Standard value (Up to)	Dry sludge	Carbonized sludge
Calorific value (kcal/kg)	5000	4,128	3,210
Fixed Carbon (%)	40	6.74	12.27
Volatility (%)	35	60.97	23.76
Ash contents (%)	30	32.29	63.99
Moisture contents (%)	10	11.41	0.9
Surface density (g/cm^2)	0.3~0.6	1.03	1.04

used as fuel as well as additive by mixing with other fuel safely.

Use of Carbonized sludge for Land Improvement

Table-9 explores possibility of application of carbonized material for land improvement. Elements found in carbonized sludge were below permissible limits of the elements allowed in stabilized material to be used as compost additive or soil conditioner in green forming. Hence carbonized material could be used safely for land improvement. Also carbonized products have physical absorption ability in addition to chemical absorption [14], hence could show effective fertilizer retaining ability in plants.

Table-9: Comparison of trace elements in carbonized sludge with allowable limits of other countries for possible utilization of carbonized product as resource promotion for land improvement.

Country	Germany	Japan	USA	Korea	Sludge in study (mg/kg)	
Parameter	mg/kg	mg/kg	mg/kg	mg/kg	Dry sludge	Carbonized sludge
Cd	5	5	85	5	0.00	0.00
Pb	900	-	840	150	0.03	0.01
Hg	8	2	57	2	0.00	0.00
Cu	800	-	4,300	300	0.03	0.04
Ni	200	-	420	50	7.44	0.16
Zn	2,000	-	7,500	900	0.44	0.16
Cr	900	-	-	300	0.60	0.06
As	-	50	75	50	0.00	0.00
Salt	-	-	-	1 %	-	-
Moisture, %	-	-	-	50	11.4	0.9

Also, it was found that the sludge carbonized products contained phosphorus in a form which plants easily absorb [15]. This is the unique property of the products that is not found in other stabilized sludge product. As the carbonized product is alkalescent and has excellent water permeability hence could improve water retaining volume of the soil effectively [16]. The pore structure of the product is believed to be suitable for the multiplication of the symbiotic microorganism and improvement in air permeability so could be suitable choice for increasing fertility of the soil.

Experimental

Carbonization Plant

The sludge used in this work was collected from an industrial wastewater treatment plant located in an industrial complex of "X" city. The plant treats a mixed type of wastewater from industries and from domestic as well. Capacity of the plant is 340000 m^3/d (domestic: 182000 m^3/d and industrial 158000 m^3/d) and sludge generation is 64.46 ton/day. The sludge was carbonized in a specially designed plant set up on laboratory scale located at 'A' area.

The carbonization plant runs at 50 kg/h operating capacity and is configured into four units: dehydrator, carbonization chamber, carbonization gas combustion and waste heat recovery, and exhaust gas treatment chamber. In dehydrator, the raw sludge with a water content of about 76 % is dried to a sludge with water content of about 25 %. The raw sludge is charged into a rotating drum where it is dried efficiently by direct contact with hot exhaust gas. The dryer which is used in this work has two unique features; first is double drum with dual rotary mode, and second is the exhaust gas system that maintains temperature up to 400-500 °C inside the drier [17]. Once the sludge is dried, the dryer exhaust gas used to dry it drops to a temperature of 200 °C which is then combusted and deodorized in the subsequent process. Dry sludge having moisture contents of about 25 % helps to reduce fuel consumption of the facility and minimizes influence of the load fluctuation of the water contents during the carbonization process in the later step [18, 19].

In carbonization chamber, the dry sludge was indirectly heated and carbonized (dry distillation) in a rotary kiln in low oxygen environment at varying temperature (350 °C, 450 °C, and 550 °C). It took about 20-30 minutes to get carbonized product of the choice. After carbonization, the char like material is produced which is cooled and humidified to prevent from spontaneous ignition and then treated as carbonized fuel. The gases from carbonization kiln and from dryer exhaust are blown with air in a combustion chamber where they are combusted at high temperature 950 °C. A part of the combustion exhaust gas is used as the heat source for indirect heating of rotary kiln. The exhaust gas of carbonization kiln is used as heat source to preheat the dryer exhaust gas before this gas is introduced into gas combustion chamber [20, 21].

In exhaust gas treatment process, the exhaust gas generated during combustion process is desulfurized and desalinized in an exhaust gas treatment tower, cooled and dehumidified, and treated for removal of soot and dust by a wet scrubber.

Leaching Test Characteristics

Leaching tests for heavy metal ions were conducted on carbonized sludge using toxicity characteristic leaching procedure (TCLP) technique [22]. Carbonized material was first crushed to a size between 5 and 50 mm. Distilled water of pH 6 was used as leaching medium. The crushed carbonized material in pH-adjusted water (solid:liquid = 1:10 by weight) was shaken for 6 hr on a magnetic stirrer and filtered with 0.45 μm filter paper. Heavy metal ions in the leachate were measured using an atomic absorption spectrophotometer (Varian Specter AA-800, Japan). Other tests were conducted using a spectrophotometer (DR/2010, HACH, USA).

Conclusions

Industrial wastewater sludge carbonized at 450 °C had the highest calorific value and the fixed carbon as well. Increase in drum speed of the dryer had nothing to do with the drying efficiency while increase in contact time of drying made dryer's operation more efficient. Carbonization at high temperature (550 °C) increased ash contents and reduced fixed carbon in the carbonized product. Emission of reduced amount of N_2O during carbonization process as compared to other sludge treatment techniques suggested carbonization a better environment friendly technique. Comparable heat contents in carbonized product with other combustible materials supported carbonized product could be utilized as fuel alone or additive fuel.

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