

【DESCRIPTION】

【Invention Title】

METHOD FOR NEUTRALIZING DREDGED SOIL WASHED WITH ACID

【Technical Field】

[1] The present invention relates to a method for neutralizing acid-washed dredged soil, and more particularly, to a method in which, after remediation of coastal dredged soil highly contaminated with heavy metals through acid washing, the dredged soil having acidity is neutralized to be reused and acid-washing liquid waste is neutralized while heavy metals originating from the soil are removed from the liquid waste by precipitation.

【Background Art】

[2] Soil or foreign matter coming from the land and deposited in a river or a harbor not only interferes with smooth flow of the river, but also can cause occurrence of bad odor due to stagnant water, aggravated flood damage, or increase in risk of grounding of ships entering and leaving the harbor. Accordingly, the deposit of soil is periodically dredged to provide environmental improvement and maintenance of sea routes.

[3] However, with the worldwide urbanization and industrial development, various types of wastewater flow into rivers and the sea, and the soil is contaminated due to precipitation of air pollutants, such as smoke emitted from factories, dumping of wastes, and application of pesticides or fertilizers, causing pollution of groundwater or river water.

[4] As a result, dredged soil can contain large amounts of pollutants having high concentrations of heavy metals as well as domestic sewage and factory wastewater depending on the region. In particular, if there is a nearby industrial complex, dredged

soil is highly likely to be contaminated with high concentrations of heavy metals.

[5] Despite the fact that contamination of dredged soil from rivers and coastal areas becomes severe, existing soil remediation technologies are inadequate for use in remediation of the dredged soil due to low remediation efficiency resulting from small particle size of the dredged soil. Therefore, there is a need for research and development of remediation technology for dredged soil highly contaminated with heavy metals.

[6] One typical method for remediation of dredged soil is disclosed in Korean Patent Laid-open Publication No. 10-2011-0130052 (published on December 5, 2011). This method provides a two-stage advanced oxidation and washing process in which application of ultra-sonication and chemical oxidation effective in separation of pollutants is conducted in two stages along with washing with a washing liquid (hydrochloric acid and EDTA). However, although this process can treat a large amount of marine dredged soil, which has high alkalinity and a large organic content, mainly consists of fine particles, and is contaminated with heavy metals, this process requires increase in treatment costs due to the use of a neutralizer for neutralizing the soil washed with strong acid, such as hydrogen peroxide.

[7] Moreover, chemicals used to wash and neutralize the contaminated soil can cause environmental problems. For example, if sodium hydroxide (NaOH) is used as the neutralizer, OH^- ions are consumed for neutralization whereas Na^+ ions remain in the soil, resulting in generation of large amounts of white crystals upon drying of the soil. This soil can cause environmental pollution due to excessive salt therein.

【Disclosure】

【Technical Problem】

[8] Embodiments of the present invention have been conceived to solve such a problem in the art and it is one aspect of the present invention to provide a method for neutralizing acid-washed dredged soil, in which dredged soil highly contaminated with various heavy metals is remediated by acid-washing, followed by neutralizing

the dredged soil having acidity, thereby allowing the remediated dredged soil to be utilized as a resource.

[9] It is another aspect of the present to provide a method for neutralizing acid-washed dredged soil, in which coal fly ash and the like, that is, industrial byproducts from thermal power plants or the like are used as a neutralizer, thereby allowing low-cost and eco-friendly neutralization of the acid-washed dredged soil.

[10] It is a further aspect of the present invention to provide a method for neutralizing acid-washed dredged soil, in which coal fly ash is mixed with process water, followed by separation into a solid substance and a liquid substance, which can be appropriately used for neutralization of the acid-washed dredged soil and the process water, thereby allowing high-efficiency neutralization of the acid-washed dredged soil.

【Technical Solution】

[11] In accordance with one aspect of the present invention, there is provided a method for neutralizing dredged soil remediated by acid washing treatment to remove contaminants therefrom, the method including: neutralizing the remediated dredged soil by adding a solid neutralizer to the remediated dredged soil in a solid phase, followed by mixing; and neutralizing used process water having been used in acid washing treatment by adding a liquid neutralizer to the used process water in a liquid phase, followed by mixing.

[12] The solid neutralizer may be coal fly ash (CFA) as byproducts of a coal combustion process.

[13] Reaction time in the neutralization step carried out by mixing the remediated dredged soil with the solid neutralizer may range from 0.5 to 1 hour. The solid neutralizer may be used in an amount of 2 wt% to 6 wt%, specifically 2 wt% to 3 wt%, based on the weight of the remediated dredged soil.

[14] The liquid neutralizer may be prepared by mixing the solid neutralizer with clean process water, followed by separating a solid substance from the mixture. Here, a weight-based mixing ratio of the solid neutralizer to the clean process water may

range from 1:90 to 1:120.

[15] The solid substance separated to prepare the liquid neutralizer may be reused as the solid neutralizer. A weight ratio of the separated solid substance to the liquid neutralizer may range from 1:90 to 1:120.

[16] Reaction time in the neutralization and precipitation step carried out by mixing the used process water with the liquid neutralizer may range from 5 to 10 minutes. The liquid neutralizer may be used in an amount of 90 vol% to 150 vol%, specifically 90 vol% to 120 vol%, based on the volume of the used process water.

[17] The method may further include: a strength enhancement step in which strength of the dredged soil is enhanced, after the neutralization step carried out by mixing the remediated dredged soil with the solid neutralizer.

[18] In the strength enhancement step, the dredged soil neutralized in the neutralization step may be mixed with coal bottom ash (CBA) as byproducts of a coal combustion process.

[19] The neutralization step carried out by mixing the used process water with the liquid neutralizer may include a precipitation step in which contaminants to be discarded are precipitated from the mixture of the spent used water and the liquid neutralizer.

【Advantageous Effects】

[20] As described above, the present invention provides a method for neutralizing acid-washed dredged soil, which can neutralize dredged soil exhibiting acidity through an acid-washing remediation process, thereby allowing the dredged soil to be reused as an available resource.

[21] In addition, the present invention provides a method for neutralizing acid-washed dredged soil, which can utilize coal fly ash and the like, which are industrial byproducts from thermal power plants or the like, as a neutralizer, thereby reducing costs required for neutralization of the acid-washed dredged soil through replacement of existing neutralizing chemicals with the industrial byproducts.

[22] Further, the present invention provides a method for neutralizing acid-

washed dredged soil, which can prepare a liquid neutralizer and a solid neutralizer through a process in which coal fly ash is mixed with clean process water, followed by liquid-solid separation, thereby allowing use of an appropriate neutralizer (the liquid neutralizer or the solid neutralizer) for each of neutralizing objects, that is, the dredged soil and the process water, and thus allowing highly efficient and eco-friendly neutralization of the acid-washed dredged soil while allowing removal of heavy metals from acid-washing liquid waste by precipitation.

【Description of Drawings】

[23] FIG. 1 is a schematic block diagram of a method for neutralizing acid-washed dredged soil according to one embodiment of the present invention.

[24] FIG. 2 is a diagram of a process of preparing a solid neutralizer and a liquid neutralizer used in neutralization of dredged soil according to one embodiment of the present invention.

【Best Mode】

[25] A method for neutralizing acid-washed dredged soil according to one embodiment of the present invention may be used to neutralize dredged soil having been subjected to washing with, for example, a strong acid such as sulfuric acid, during a remediation process of the dredged soil highly contaminated with various heavy metals.

[26] Hereinafter, the method for neutralizing acid-washed dredged soil according to one embodiment of the present invention will be described in detail with reference to the accompanying drawings.

[27] Referring to FIG. 1, the method for neutralizing acid-washed dredged soil according to one embodiment of the present invention may be used to neutralize remediated dredged soil 3 and spent process water 4, which are resultants of a remediation step S10 in which dredged soil 1 highly contaminated with various heavy metals is washed with, for example, an acid washing liquid 2 prepared using a strong

acid such as sulfuric acid.

[28] The highly contaminated dredged soil 1 is washed to a degree meeting cleanup standards by acid washing (acid leaching). However, since the remediated dredged soil 3 has strong acidity, it is necessary to neutralize the remediated dredged soil in order to reuse the remediated dredged soil. After neutralization, the dredged soil may be subjected to strength enhancement treatment, as needed. In addition, the used process water 4, that is, process water having been put to use in the contaminated dredged soil 1 remediation step S10, also has strong acidity, and thus needs to be neutralized so as to be reused.

[29] According to this embodiment, in order to neutralize the remediated dredged soil 3 (water content: about 75%), that is, dredged soil having been subjected to acid washing during the process of purifying the contaminated dredged soil 1, coal fly ash (CFA), which is a byproduct of a coal combustion process in a thermal power plant or the like, is used as a neutralizer. Accordingly, it is possible to reduce neutralizer-related costs. More specifically, a solid neutralizer, for example, solid CFA 11, may be used for neutralization of the remediated dredged soil 3.

[30] According to this embodiment, in addition to the remediated dredged soil 3, the used process water 4, that is, used process water having been used in acid washing, may also be neutralized. A liquid neutralizer, for example, liquid CFA 12, may be used for neutralization of the used process water 4.

[31] The use of a neutralizer in the same phase as a neutralizing object can shorten the reaction time for neutralization and thus the overall treatment time. That is, when either a neutralizing object or a neutralizer is a solid, the reaction time for neutralization is longer than when both the neutralizing object and the neutralizer are liquids. Accordingly, when the two reactants have the same phase, it is possible to shorten the reaction time for neutralization. In addition, when a solid is mixed and reacted with a liquid, a solid-liquid separation process for phase separation is required after completion of the reaction. Accordingly, when the two reactants have the same phase, it is possible to advantageously reduce the overall treatment time.

[32] Since the coal fly ash, which is a byproduct from a power plant or the like, is in a solid phase, the coal fly ash may thus be used as the solid neutralizer, that is, the

solid CFA 11.

[33] Referring to FIG. 2, the liquid CFA 12 may be prepared by mixing the solid CFA 11 with clean process water 14 (for example, distilled water), followed by solid-liquid separation. Here, a mixing ratio of the solid CFA to the clean process water may vary depending on the pH of dredged soil to be neutralized. For example, when the dredged soil to be neutralized has a pH of about 2.8, a weight-based mixing ratio of the solid CFA 11 to the clean process water 14 may range from about 1:90 to 1:120. For example, a weight-based mixing ratio of the solid CFA 11 to the clean process water 14 may be about 1:100.

[34] Through solid-liquid separation of a mixed solution of the solid CFA 11 and the clean process water 14, the solid CFA and the liquid CFA 12 (that is, an aqueous solution of CFA) are obtained. Here, the solid CFA 11 obtained through the solid-liquid separation process may be reused. The solid CFA and the liquid CFA obtained through the solid-liquid separation process may each constitute half of the alkalinity of the mixed solution. For example, the solid CFA may have an alkalinity of about 50% (2,417 mg/L CaCO_3) and the liquid CFA may have an alkalinity of about 50% (2,774 mg/L CaCO_3). A weight ratio of the solid CFA to the liquid CFA may range from about 1:90 to 1:120. For example, a weight ratio of the solid CFA to the liquid CFA may be about 1:100.

[35] Referring to FIG. 1 again, the reaction time in a neutralization step S20 carried out by mixing the remediated dredged soil 3 with the solid CFA 11 may range from about 0.5 to 1 hour. For example, when dredged soil to be neutralized has a pH of about 2.8, the neutralizer, that is, the solid CFA, may be used in an amount of about 2 wt% to 6 wt%, specifically 2 wt% to 3 wt%, based on the weight of the dredged soil. If the reaction time is less than 0.5 hours, the neutralization reaction is not completed, causing continuous increase in pH, whereas, if the reaction time is more than 1 hour, the neutralization reaction can be completed, but treatment time is lengthened, causing reduction in economic feasibility. If the amount of the solid CFA is less than 2 wt% based on the weight of the dredged soil, the dredged soil can be insufficiently neutralized, whereas, if the amount of the solid CFA is more than 6 wt% based on the weight of the dredged soil, neutralizer consumption is excessively high and the

neutralized dredged soil can have alkalinity. The above values are calculated on the assumption that the dredged soil to be neutralized has a pH of about 2.8, and thus may be varied with varying pH of the dredged soil to be neutralized.

[36] The dredged soil having been neutralized through the neutralization step S20 may be reused without any further process, or may be reused after being enhanced in strength through a strength enhancement step S30. In the strength enhancement step S30, coal bottom ash (CBA) 13, which is a byproduct of a coal combustion process in a thermal power plant or the like, may be mixed with the dredged soil so as to enhance the strength of the dredged soil. The dredged soil mixed with CBA 13 has enhanced strength and thus can be reused in a wider variety of applications, such as reclamation in harbors or coastal areas.

[37] In a neutralization and precipitation step S40, the used process water 4 may be treated by mixing with the liquid CFA 12. The reaction time in the neutralization and precipitation step S40 carried out by mixing the used process water 4 with the liquid CFA 12 may range from about 5 to 10 minutes. The neutralizer, that is, the liquid CFA, may be used in an amount of 90 vol% to 150 vol% based on the volume of the used process water. If the reaction time is less than 5 minutes, the neutralization reaction is not completed, causing continuous decrease in pH, whereas, if the reaction time is more than 10 minutes, the neutralization reaction can be completed, but the treatment time is lengthened, causing reduction in economic feasibility. In addition, if the amount of the liquid CFA is less than 90 vol% based on the volume of the dredged soil, the dredged soil can be insufficiently neutralized, whereas, if the amount of the liquid CFA is more than 150 vol% based on the volume of the dredged soil, neutralizer consumption is excessively high and the neutralized process water can have alkalinity.

[38] The process water neutralized through the neutralization and precipitation step S40 may be reused, whereas a precipitate separated from the mixed solution of the used process water and the liquid CFA may be retreated or discarded. Since the precipitate originates from heavy metals removed from the dredged soil, rather than from the dredged soil, the amount of discarded precipitate is insignificant (for example, about 0.001%), as compared with the total amount of treated dredged soil.

[39] Table 1 shows the properties of the contaminated dredged soil 1 before acid

washing treatment, the remediated dredged soil 3 after acid washing treatment, and industrial byproducts used as the solid neutralizers in the neutralization step, that is, the solid CFA 11 and the solid CBA.

[40] Table 1

Sample		pH	Cu	Zn	Cr	Ni	Cd	Pb	As
			(mg/kg)						
Contamination level			190	2,000	380	210	14.0	580	85
Cleanup level			190	720	180	100	4.3	530	76
Contaminated dredged soil	Sample 1	8.50	1,978	2,636	192	110	9.0	244	91
	Sample 2	8.53	1,583	2,070	208	112	6.0	187	45
	Sample 3	8.19	1,637	2,108	185	115	7.0	258	52
	Sample 4	8.29	1,659	2,167	218	130	7.0	318	52
	Average		1,714	2,245	201	117	7.3	252	60
Remediated dredged soil	Sample 1-1	2.87	139	170	50	19	2	76	40
	Sample 1-2		176	259	47	25	2	41	35
	Sample 2-1	2.76	69	89	31	15	1	28	20
	Sample 2-2		83	124	34	17	1	13	22
	Sample 3-1	2.81	96	131	36	16	1	23	25
	Sample 3-2		87	103	31	15	1	30	30
	Sample 4-1	2.86	147	242	52	24	1	24	31
	Sample 4-2		109	121	38	19	2	96	31
	Average	2.83	113	155	40	19	1	41	29
Industrial	CFA #1	12.36	116	128	35.2	66.5	5.5	17.2	23.8

byproduct	CFA #2	12.37	112	120	36.1	69.7	5.9	15.7	21.4
	CBA #1	11.08	35	68	7.7	15.4	0.5	<0.75	<1.2

[41] As can be seen from Table 1, the remediated dredged soil obtained by subjecting the contaminated dredged soil to acid washing meets the cleanup standard. According to this embodiment, in order to neutralize the remediated dredged soil, which meets the cleanup standard, industrial byproducts having alkalinity (solid neutralizers) were used. Since the concentration of each heavy metal in the byproducts is below a cleanup level, there is no concern of contamination of the remediated dredged soil with the byproducts. Here, the Dutch Standard, which is used worldwide, was used as the cleanup standard.

[42] Table 2 shows results of neutralizing the remediated dredged soil using the industrial byproducts shown in Table 1.

[43] Table 2

Amount of CFA based on weight of acid-washed dredged soil (wt%)	pH	
	CFA	CBA
0	2.83	
0.5	3.39	3.13
1	4.5	3.45
2	5.95	3.74
3	6.59	3.91
5	7.38	4.15
6	7.56	4.24
10	8.65	4.65
15	9.38	5.14
20	10.18	5.57
30	10.98	6.01

[44] Referring to Table 2, it can be seen that the industrial byproducts had different levels of neutralizing ability and the solid CFA had better neutralizing ability than the solid CBA. In addition, when the solid CFA was used in an amount of about 2 wt% to 3 wt% based on the weight of the dredged soil (slurry) remediated by acid washing, the neutralized dredged soil had a neutral pH.

[45] Table 3 shows the properties of the used process water 4 having been used in

acid washing and industrial byproducts used as the liquid neutralizers in the neutralization and precipitation step, that is, the liquid CFA 12 and the liquid CBA.

[46] Table 3

Sample	pH	Cu	Zn	Cr	Ni	Cd	Pb	As
		(mg/kg)						
Used process water	2.83	74.05	84.75	4.93	4.935	0.255	4.36	0.86
CFA solution	12.36	0.002	0.013	0.05	-	0.001	-	0.032
CBA solution	11.08	0.002	0.006	0.008	-	-	-	0.012

[47] As can be seen from Table 3, the used process water separated from the acid-washed dredged soil had a pH of about 2.83. According to this embodiment, in order to neutralize the used process water, the liquid CFA (that is, the CFA solution) having better neutralizing ability was used. As in the case of the solid neutralizers, since the concentration of each heavy metal in the liquid neutralizers was below the cleanup level, there is no concern of contamination of the used process water with the liquid neutralizers.

[48] Table 4 shows results of neutralizing the used process water using the industrial byproduct (CFA solution) shown in Table 3.

[49] Table 4

Amount of CFA solution (ml)	Process water (ml)	pH	Cu	Zn	Cr	Ni	Cd	Pb	As
			(mg/kg)						
0	50	2.83	74.05	84.75	4.935	4.93	0.255	4.36	0.86
11		3	12.28	13.62	0.62	0.8	0.03	0.63	0.04
28		4	9.38	11.07	0.08	0.64	0.02	0.28	0.02
45		5.5	3.97	9.52	0.041	0.55	0.02	-	0.01
60		6.2	0.07	0.58	0.02	0.25	0	-	0.01
68		7.6	0.06	0.03	0.03	0.02	-	-	0.01
75		8.5	0.06	0.01	0.04	0.01	-	-	0.01
85		10	0.06	0.01	0.04	0	-	-	0.01

[50] Referring to Table 4, it can be seen that the CFA solution (liquid CFA) could neutralize the used process water while reducing the contaminant concentration in the used process water through precipitation of heavy metals from the used process water.

[51] Although some embodiments have been described herein, it should be understood that these embodiments are provided for illustration only and are not to be construed in any way as limiting the present invention, and that various modifications, changes, alterations, and equivalent embodiments can be made by those skilled in the art without departing from the spirit and scope of the invention.

【CLAIMS】

【Claim 1】

A method for neutralizing dredged soil remediated by acid washing treatment to remove contaminants therefrom, the method comprising:

neutralizing the remediated dredged soil by adding a solid neutralizer to the remediated dredged soil in a solid phase, followed by mixing; and

neutralizing used process water having been used in acid washing treatment by adding a liquid neutralizer to the used process water in a liquid phase, followed by mixing.

【Claim 2】

The method according to claim 1, wherein the solid neutralizer is coal fly ash (CFA) as byproducts of a coal combustion process.

【Claim 3】

The method according to claim 1, wherein reaction time in the neutralization step carried out by mixing the remediated dredged soil with the solid neutralizer ranges from 0.5 to 1 hour.

【Claim 4】

The method according to claim 1, wherein the solid neutralizer is used in an amount of 2 wt% to 6 wt% based on the weight of the remediated dredged soil.

【Claim 5】

The method according to claim 1, wherein the liquid neutralizer is prepared by mixing the solid neutralizer with clean process water, followed by separating a

solid substance from the mixture.

【Claim 6】

The method according to claim 5, wherein a weight-based mixing ratio of the solid neutralizer to the clean process water ranges from 1:90 to 1:120.

【Claim 7】

The method according to claim 5, wherein the solid substance separated to prepare the liquid neutralizer is reused as the solid neutralizer.

【Claim 8】

The method according to claim 5, wherein a weight ratio of the separated solid substance to the liquid neutralizer ranges from 1:90 to 1:120.

【Claim 9】

The method according to claim 1, wherein reaction time in the neutralization and precipitation step carried out by mixing the used process water with the liquid neutralizer ranges from 5 to 10 minutes.

【Claim 10】

The method according to claim 1, wherein the liquid neutralizer is used in an amount of 90 vol% to 150 vol% based on the volume of the used process water.

【Claim 11】

The method according to claim 1, further comprising:

a strength enhancement step in which strength of the dredged soil is enhanced, after the neutralization step carried out by mixing the remediated dredged soil with the solid neutralizer.

【Claim 12】

The method according to claim 11, wherein, in the strength enhancement step, the dredged soil neutralized in the neutralization step is mixed with coal bottom ash (CBA) as byproducts of a coal combustion process.

【Claim 13】

The method according to claim 1, wherein the neutralization step carried out by mixing the used process water with the liquid neutralizer comprises a precipitation step in which contaminants to be discarded are precipitated from the mixture of the used process water and the liquid neutralizer.