

METHOD UTILIZING INDUSTRIAL FLUE GAS FOR REMOVING METAL IONS FROM RICE HULLS

FIELD OF THE INVENTION

[0001] The invention relates to the recycling of rice hull, and more particularly to a method for removal of metal ions from rice hull by utilizing industrial flue gas.

BACKGROUND OF THE INVENTION

[0002] China stands first in the world for rice production. The rice planting area was about 430 million mu in 2008, and the total output was about 189 million tons, which can produce nearly 40 million tons of rice hull. In the world, the annual total output of the rice hull is more than 68 million tons. The rice hull includes water, organic matter (lignin, cellulose, and hemicellulose), amorphous silica, and a small amount of metal ions.

Conventionally, the rice hull is ground into chaff for use as feeds. With the development of science and technology, the rice hull is used for power generation, for producing oil and nano products, particularly, for preparation of nano silica.

[0003] A typical method for producing silica from the rice hull includes: boiling the rice hull with strong acid (e. g. hydrochloric acid, sulfuric acid, nitric acid, and so on), and washing in ultrapure water; calcining the rice hull to remove most of impurities; soaking the rice hull in the strong acid and rewashing using the high pure water, for further reducing the impurity content; drying the rice hull, transporting to a biomass power plant for combustion or chemically thermal decomposition, to yield nano silica.

[0004] The above method for removing metal ions from rice hull involves strong acids.

Strong acids are harmful to human body and pollutes environment. In addition, the waste water resulting from the acid treatment cannot be drained off directly, thereby increasing the disposal cost.

SUMMARY OF THE INVENTION

[0005] In view of the above-described problems, it is one objective of the invention to a method for removal of metal ions from rice hull by utilizing industrial flue gas that features high efficiency, environmental friendliness, and economy.

[0006] To achieve the above objective, in accordance with one embodiment of the invention, there is provided a method for removal of metal ions from rice hull by utilizing industrial flue gas. The method comprises the following steps: 1) providing a water storage reactor, and disposing a gas dispersion device at a bottom of the water storage reactor; 2) bagging rice hull and placing in the water storage reactor, and pressing down the bagged rice hull below a water surface of the water storage reactor; 3) spraying industrial flue gas into the water storage reactor via the gas dispersion device; controlling the amount of the industrial flue gas such that the amount of carbon dioxide dissolved in per 100 g of water is about 1 g whereby generating a carbonic acid solution; 4) allowing the carbonic acid solution to react with a metal ion of the rice hull to yield a precipitate; 5) washing the rice hull collected in step 4), washing again with desalinated water, and squeezing the rich hull, whereby removing the metal ion from the rice hull.

[0007] Preferably, the water storage reactor has a depth of between 6 and 10 m. Appropriate depth of the water storage reactor can ensure the carbon dioxide in the industrial flue gas is sufficiently dissolved in the water to yield a carbonic acid solution with a certain concentration.

[0008] Preferably, the gas dispersion device comprises a gas orifice configured to horizontally or vertically agitate water to form vortexes, and the industrial flue gas is sprayed from the gas orifice. The vortexes of the water can improve the degree of dispersion of carbon dioxide in the water thereby facilitating the formation of carbonic acid. The gas orifice can be multiple in annular distribution, and sprays gas outward along a tangential direction.

[0009] Preferably, the gas orifice is at least 1.5 m higher than the bottom of the water storage reactor. The carbonic acid reacts with the rice hull to yield the precipitate. To prevent the precipitate from blocking the gas orifice, the gas orifice is at least 1.5 m higher than the bottom of the water storage reactor.

[0010] Preferably, the gas orifice has a pore size of between 0.005 and 0.012 mm. The spray of the gas from the gas orifice satisfies the Laplace's equation, that is to say, additional pressure on the spherical surface is proportional to the surface tension coefficient and is inversely proportional to the radius of the spherical radius. When the surface tension coefficient is constant, the smaller the radius, the greater the additional pressure. The smaller the gas orifice, the smaller the sprayed bubbles. When small bubbles of carbon dioxide are sprayed from the gas orifice, the bubbles expand, and the surface tension decreases rapidly, the bubbles burst, thus increasing the contact area of the carbon dioxide with the water, and accelerating the formation of carbonic acid.

[0011] Preferably, the gas dispersion device further comprises a plurality of microporous aerators, and the industrial flue gas is sprayed from the microporous aerators. The microporous aerators are configured to improve the dissolution of carbon dioxide in the water.

[0012] The present disclosure also provides another method for removal of metal ions from rice hull by utilizing industrial flue gas. The method comprises the following steps:1)

providing a reaction tank, the reaction tank comprising a gas distributor disposed at a lower part thereof and a liquid distributor disposed at an upper part thereof, wherein, the gas distributor comprises microporous aerators, a recycle liquid outlet is disposed on a wall of the reaction tank below the gas distributor, a gas outlet is disposed at a top of the reaction tank, and a precipitate outlet is disposed at a bottom of the reaction tank;2) filling the reaction tank with rice hull and water, closing the gas outlet, and allowing the industrial flue gas to be sprayed from the microporous aerators of the gas distributor;3) allowing carbon dioxide in the industrial flue gas to be dissolved in the water, 4 g of carbon dioxide per 100 g of water, to yield a carbonic acid solution; 4) allowing the carbon acid solution to react with a metal ion of the rice hull to yield a precipitate; and5) washing the rice hull collected in step 4), washing again with desalinated water, and squeezing the rich hull, whereby removing the metal ion from the rice hull.

[0013] The principle of the method for removal of metal ions from rice hull by utilizing industrial flue gas is summarized as follows. Carbon dioxide in the industrial flue gas is dissolved in water to yield carbonic acid which is used to acidify rice hull where carbonic acid reacts with metal ions such as aluminum, calcium, magnesium, iron, manganese to yield corresponding insoluble salts. The precipitates are a carbonate or an oxide of the metal. Thus, the metal ions of the rice hull can be efficiently removed. Carbon dioxide is a nonpolar molecule, but it is soluble in a strong polar solvent, and the dissolubility thereof is related to the temperature, the pressure, and the properties of the solvent. With the increase of temperature, the dissolubility of carbon dioxide decreases. At normal temperature and pressure, the carbon dioxide volume and the water volume in a saturated aqueous solution is almost 1: 1. Most of the carbon dioxide is weakly bound to water molecule to form a hydrate molecule, and only a small part of the carbon dioxide participates in the formation of carbonic acid. Low concentration of carbonic acid cannot treat a large amount of rice hull. When the pressure of carbon dioxide is less than 0.5

MPa, the dissolubility is proportional to the pressure; when the pressure exceeds 0.5 MPa, due to the formation of carbonic acid, with the increase of the pressure, the dissolubility of carbon dioxide increases rapidly. Thus, to improve the concentration of carbonic acid in water so as to remove the metal ions in the rice hull, it is a key element to increase the carbon dioxide pressure.

[0014] There are three ways to improve the balance pressure of carbon dioxide on the liquid surface. The first is to make use of water pressure, the second is to dispose a gas dispersion device, and the third is to increase the gas pressure on the liquid surface in an enclosed tank. One method of the present disclosure is to dispose a water storage reactor which makes use of the water pressure and the gas dispersion device to improve the dissolubility of carbon dioxide in water. Another method of the present disclosure is to dispose a reaction tank which makes use of an enclosed space to improve the carbon dioxide pressure on the liquid surface, thereby facilitating the dissolution of carbon dioxide.

[0015] The method of the present disclosure involving the water storage reactor can treat a large amount of rice hull for one cycle, and the involved equipment is simple and easy for operation. The method can remove the metal ions and dusts of the rice hull, so it is particularly suitable for primary tough treatment.

[0016] The method of the present disclosure involving the reaction tank has controllable reaction conditions, high carbon dioxide solubility, and high efficiency, which is particularly suitable for secondary fine treatment.

[0017] Compared with conventional methods for removal of metal ions using a strong acid, the present disclosure has the following advantages:

[0018] 1. The carbonic acid has weak acidity, and poses little pollution to environment.

Carbon dioxide from the industrial flue gas comprising power plant flue gas or exhaust gas is utilized for the removal of metal ions from the rice hull, which saves the costs and prevents the environmental pollution. A biomass power plant equipped with 12 MW plant unit produces 678 thousand tons of industrial flue gas annually, based on the carbon dioxide percentage of about at least 10%, the carbon oxide content is about 67.8 thousand tons. Making full use of the carbon dioxide will produce considerable economic value.

[0019] 2. The acidification of the rice hull produces a precipitate and a solution comprising soluble substances such as sodium, potassium, nitrogen, phosphorus, sulfur. The solution can be used as a direct nutrient solution for plant cultivation. The precipitate can be used as a construction material or an additive, which poses no pollution. Strong acid used in conventional methods tends to pollute environment, and the recycling cost is pretty high.

[0020] 3. After being washed twice, squeezed using desalinated water, and dried, the acidified rice hull can be directly transported to a biomass power plant for combustion or thermal decomposition to yield nano silica. If the rice hull is treated by strong acid, the high temperature calcination is required, followed by soaking in strong acid and washing by high purity water, and then drying, which is very complex.

[0021] Thus, in the present disclosure, the industrial flue gas is introduced to water where carbon dioxide is dissolved in the water to yield carbonic acid. The carbonic acid reacts with the rice hull soaked in the water whereby removing the metal ions. After being washed and dried, the treated rice hull can be directly transported to a biomass power plant for combustion or thermal decomposition, no need of high temperature calcination, to yield nano silica. The method reuses the industrial flue gas, reduces the emissions, so it is environmentally friendly, and has low pollution, low energy consumption, high efficiency.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] FIG. 1 is a sectional view of a water storage reactor in according to one embodiment of the invention;

[0023] FIG. 2 is a top view of a water storage reactor in FIG. 1; and

[0024] FIG. 3 is a sectional view of a reaction tank in according to one embodiment of the invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0025] For further illustrating the invention, experiments detailing a method for removal of metal ions from rice hull by utilizing industrial flue gas are described below. It should be noted that the following examples are intended to describe and not to limit the invention.

Example 1

[0026] As shown in FIGS. 1-2, a method for removal of metal ions from rice hull by utilizing industrial flue gas is described as follows.

[0027] 1. A water storage reactor **1** having a depth of 7 m and a length and width respectively of 100 m was provided. 25 gas dispersion devices **2** for introducing industrial flue gas were disposed at the bottom of the water storage reactor **1**. The gas dispersion devices **2** comprised a gas orifice (not shown in the drawings) configured to horizontally or vertically agitate water to form vortexes. The industrial flue gas was sprayed from the gas orifice. The gas orifice was 1.5 m higher than the bottom of the water storage reactor, and had a pore size of 0.01 mm. The gas dispersion devices

2further comprised a plurality of microporous aerators, and the industrial flue gas was sprayed from the microporous aerators.

[0028] 2. The rice hull 5was bagged, placed in the water storage reactor1, and pressed down using press bars to be lower than the water surface of the water storage reactor.

[0029] 3. The industrial flue gas released from a biomass power plant was filtered by dust collecting equipment, and received by a gas main4which was connected to the gas dispersion devices. The industrial flue gas was sprayed into the water with depth of 5.5 m via the gas dispersion devices2. Under such conditions, the dissolution amount of carbon dioxide in the water was increased by 5 folds compared with that under normal temperature and pressure, that is, 1 g of carbon dioxide was dissolved in per 100 g of water. Thus, a carbonic acid solution was obtained, which was adapted to acidify the rice hull 5. The metal ion of the rice hull reacted with the carbonic acid solution to yield a precipitate. Thereafter, the rice hull 5 was washed, and squeezed with desalinated water, whereby removing the metal ion of the rice hull5.

[0030] Besides the precipitate, the acidification of the rice hull also produced a solution. The solution was rich in nitrogen, phosphorus, potassium, sodium, and small organic molecules. The precipitate was mainly a carbonate and oxide of a metal such as aluminum, calcium, magnesium, iron, and manganese. The insoluble substances and the dust in the industrial flue gas precipitated in the bottom of the water storage reactor. The treatment period for the rice hull lasted for 6 days. Then, the rice hull was washed twice, and then desalinated water added, and squeezed. After such steps, between 60 and 75% of metal ions were removed. For each cycle, the treatment amount of the rice hull can reached about 2500 tons.

Example 2

[0031] As shown in FIG. 3, a method for removal of metal ions from rice hull by utilizing industrial flue gas is described as follows.

[0032] A reaction tank **13**, having a height of 15 m and an inside capacity of 1000 m³, was provided. A gas distributor **7** comprising microporous aerators was disposed at the lower part of the reaction tank **13**. A recycle liquid outlet **6** was disposed on the wall of the reaction tank **13** below the gas distributor **7**. A gas outlet **10** was disposed at the top of the reaction tank **13**, and a cone was disposed at the bottom of the reaction tank for collecting precipitates. At the bottom of the cone, a precipitate outlet **8** was disposed. A demister **12** and a liquid distributor **11** were disposed at the upper part of the reaction tank **13**. The demister **12** was disposed above the liquid distributor **11**.

[0033] Firstly, the reaction tank **13** was filled with rice hull and water. The rice hull was floated on the water surface, and was below the liquid distributor **11**. The gas outlet **10** was closed. The industrial flue gas was sprayed from the microporous aerators of the gas distributor **7**. Under such conditions, the pressure of the industrial flue gas in the reaction tank **13** increased rapidly. The dissolution amount of carbon dioxide in the water was increased by 20 folds compared with that under normal temperature and pressure, that is, 4 g of carbon dioxide was dissolved in per 100 g of water. Thus, a carbonic acid solution was obtained, which was adapted to acidify the rice hull **5**. The carbonic acid solution was sprayed on the rice hull **5** from the liquid distributor **11**, so that the metal ion of the rice hull reacted with the carbonic acid solution to yield a precipitate. Thereafter, the rice hull **5** was washed, and squeezed with desalinated water, whereby removing the metal ion from the rice hull **5**.

[0034] After such steps, 80% of metal ions were removed. For each cycle, the treatment amount of the rice hull can reached about 100 tons.

[0035] If the water storage reactor **1** in Example **1** and the reaction tank in Example **2** were

combined for use, that is, the water storage reactor **1** is used for primary treatment, and the reaction tank **3** is used for secondary treatment, and the resulting rice hull is washed and squeezed using desalinated water thrice, then 90% of metal ions are removed.

[0036] Metal residues in the rice hull after being treated by method in example **1**, example **2**, and a combination thereof are listed in Table **1**.

Table 1

Sample	Elements	Components (%)												Metal content
		SiO ₂	Al	Fe	Mn	Mg	Ca	Cu	Zn	Ti	K	Na	others	
Raw rice hull		80.5	3.80	0.44	0.2	2.71	3.56	0.027	0.003	0.31	2.8	1.53	4.12	15.38
Method in Example 1	Content	88.3	1.3	0.2	0.1	1.0	1.1	0.025	0.002	0.2	1.4	1	2.4	6.33
Method in Example 2	(wt. %)	94.7	0.7	0.18	0.06	0.5	0.6	0.015	0.001	0.15	0.5	0.6	2	3.30
Combination thereof		97.5	0.4	0.1	0.03	0.2	0.2	0.01	0	0.1	0.2	0.3	1	1.54

[0037] As shown in the above table, the method of the invention exhibits the same removal effect of metal ions from rice hull by utilizing industrial flue gas as by utilizing strong acid, and the resulting rice hull can absolutely meet the requirement for preparation of silica for a biomass power plant.

CLAIMS

1. A method for removal of metal ions from rice hull by utilizing industrial flue gas, the method comprising:
 - 1) providing a water storage reactor (1), and disposing a gas dispersion device (2) at a bottom of the water storage reactor;
 - 2) bagging rice hull and placing in the water storage reactor (1), and pressing down the bagged rice hull below a water surface of the water storage reactor;
 - 3) spraying industrial flue gas into the water storage reactor via the gas dispersion device (2); controlling the amount of the industrial flue gas such that the amount of carbon dioxide dissolved in per 100 g of water is about 1 g, whereby generating a carbonic acid solution;
 - 4) allowing the carbonic acid solution to react with a metal ion of the rice hull to yield a precipitate;
 - 5) washing the rice hull (5) collected in step 4), washing again with desalinated water, and squeezing the rich hull (5), whereby removing the metal ion from the rice hull (5).
2. The method of claim 1, **characterized in that** the water storage reactor (1) has a depth of between 6 and 10 m.
3. The method of claim 2, **characterized in that** the gas dispersion device (2) comprises a gas orifice configured to horizontally or vertically agitate water to form vortexes, and the industrial flue gas is sprayed from the gas orifice.

4. The method of claim 3, **characterized in that** the gas orifice is at least 1.5 m higher than the bottom of the water storage reactor.
5. The method of claim 4, **characterized in that** the gas orifice has a pore size of between 0.005 and 0.012 mm.
6. The method of any one of claims 1-4, **characterized in that** the gas dispersion device (2) further comprises a plurality of microporous aerators, and the industrial flue gas is sprayed from the microporous aerators.
7. A method for removal of metal ions from rice hull by utilizing industrial flue gas, the method comprising:
 - 1) Providing a reaction tank (13), the reaction tank (13) comprising a gas distributor (7) disposed at a lower part thereof and a liquid distributor (11) disposed at an upper part thereof, wherein, the gas distributor (7) comprises microporous aerators, a recycle liquid outlet (6) is disposed on a wall of the reaction tank (13) below the gas distributor (7), a gas outlet (10) is disposed at a top of the reaction tank (13), and a precipitate outlet (8) is disposed at a bottom of the reaction tank (13);
 - 2) filling the reaction tank (13) with rice hull (5) and water, closing the gas outlet (10), and allowing the industrial flue gas to be sprayed from the microporous aerators of the gas distributor (7);
 - 3) allowing carbon dioxide in the industrial flue gas to be dissolved in the water, 4 g of carbon dioxide per 100 g of water, to yield a carbonic acid solution;
 - 4) allowing the carbon acid solution to react with a metal ion of the rice hull to yield a precipitate;
 - 5) washing the rice hull (5) collected in step 4), washing again with desalinated

water, and squeezing the rich hull (5), whereby removing the metal ion from the rice hull (5).