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TITLE OF INVENTION

54	POROUS MEDIA FOR AUTOTROPHIC DENITRIFICATION USING SULFUR

57	ABSTRACT (NOT MORE THAT 150 WORDS)	NUMBER OF SHEETS	16

If no classification is finished, Form P.9 should accompany this form
The figure of the drawing to which the abstract refers is attached.

【ABSTRACT】

Provided is a porous medium for autotrophic denitrification using sulfur. More specifically, the present invention provides a porous medium for autotrophic denitrification using sulfur for water treatment, which is prepared by: adding inexpensive alkalinity agent such as limestone and mollusk shells to powdered sulfur, adding pulverized rock wool from agricultural waste and nutrients needed for the growth of denitrifying bacteria, and mixing well the same; heating the resultant mixture to 130-150 °C, and mixing well to obtain homogeneous slurry; and slowly cooling the resultant slurry with cold water.

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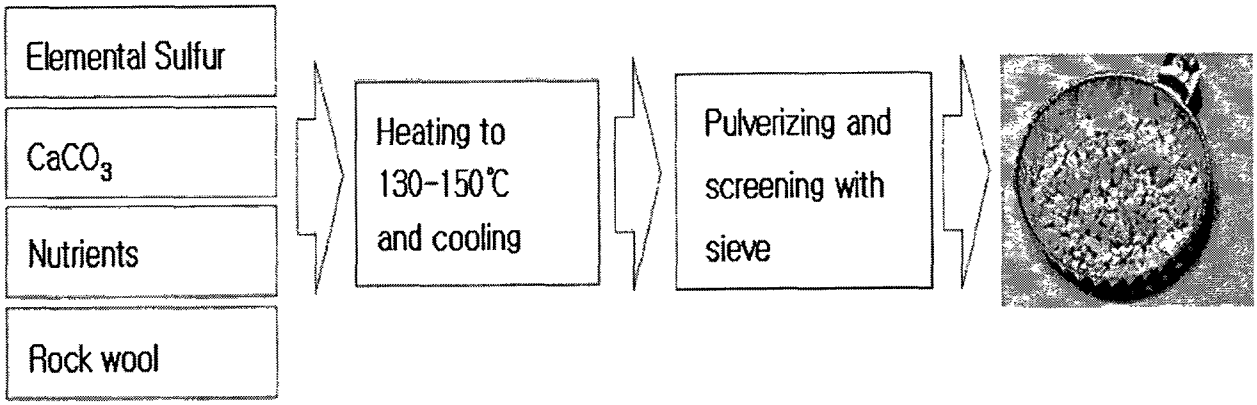
【FIG. 1】



【Technical Field】

The present invention relates to a porous medium for autotrophic denitrification using sulfur, more particularly to a porous medium for autotrophic denitrification using sulfur for water treatment, which comprises powdered sulfur, alkalinity agent, pulverized rock wool and nutrients needed for the growth of denitrifying bacteria.

The present invention further relates to a preparation method of an improved sulfur medium making the provision of alkalinity and attachment of bacteria at early stage easier in treating groundwater, leachate, sewage or wastewater containing low-concentration nitrate nitrogen with denitrifying bacteria using sulfur.

【Background Art】

A stoichiometric equation for autotrophic denitrification reaction using sulfur is described in Scheme 1 below. Differently from heterotrophic denitrification, no external organic carbon source is required. However, the alkalinity decreases because hydrogen ion is created. Further, in case of groundwater, attachment and growth of the denitrifying bacteria using sulfur may be inhibited due to lack of the nutrients.

[Scheme 1]

Autotrophic denitrification using sulfur

$$55S + 20CO_2 + 50NO_3^- + 38H_2O + 4NH_4^+ \rightarrow 4C_5H_7O_2N + 25N_2 + 55SO_4^{2-} + 64H^+$$

In the conventional autotrophic denitrification using sulfur, powdered sulfur is packed in a column and $CaCO_3$ containing materials such as limestone or mollusk shells are packed in the column as alkalinity agent. The materials serve as at once

inorganic carbon source and source of alkalinity. As seen in FIG. 3a, powdered has smooth and hydrophobic surface. Therefore, a long time is required for attachment and growth of bacteria on the sulfur particles. When using a sulfur-packed reactor, typically spherical particulate sulfur with a particle size from 2-7 mm is used. Hence, even after screening of sulfur, the average size is smaller than 10 mm. It is because most of commercially available sulfur has a small size, and such small-sized sulfur is used in the conventional denitrification using sulfur.

Such small-sized particulate sulfur results in very small porosity when applied for a packing type reactor. Upon denitrification, the biofilm formed by the bacteria attached to sulfur particles becomes thicker, and the pores through which water can pass become even smaller. Consequently, hydraulic head loss increases and supply of nutrients to bacteria becomes difficult due to local blockage as time goes by, thereby resulting in reduction of treatment efficiency. Further, along with the consumption of sulfur, particle size of sulfur may decrease further and the alkalinity source packed in the reactor, including limestone and $CaCO_3$, may be dissolved, thereby blocking the reactor. To solve this problem, back washing is performed periodically. However, the back washing results in transient aerobic condition, although it does not last for a long time, which interferes with the growth of the bacteria favoring anaerobic. Further, a large amount of sulfur and $CaCO_3$ may be lost during the back washing.

【Disclosure】

The present invention has been made in an effort to solve the above-described problems associated with the prior art. The inventors of the present invention have found that a porous medium comprising powdered sulfur, limestone, rock wool and

nutrients needed for the growth of denitrifying bacteria is useful in a biological denitrification process for treating groundwater containing nitrate nitrogen.

Accordingly, a major object of the present invention is to provide a porous medium for autotrophic denitrification using sulfur with increased specific surface area for enhancing biological denitrification and a method for preparing the same.

【Description of Drawings】

FIG. 1 schematically illustrates the process of preparing the porous medium according to the present invention.

FIG. 2 schematically illustrates the improved porous medium according to the present invention.

FIG. 3a is the SEM photograph showing the surface of a medium comprising sulfur only.

FIG. 3b is the SEM photograph showing the surface of a medium comprising sulfur and $CaCO_3$ only.

FIG. 3c is the SEM photograph showing the surface of the improved porous medium according to the present invention.

【Best Mode】

Reference will now be made in detail to the preferred embodiments of the present invention.

In an embodiment, the present invention provides a porous medium for autotrophic denitrification using sulfur for water treatment, which comprises powdered

sulfur, alkalinity agent, pulverized rock wool and nutrients needed for the growth of denitrifying bacteria.

As used herein, the term "autotrophic denitrification" refers to a denitrification process using bacteria that do not require an organic material as electron donor. In heterotrophic denitrification, denitrification is carried out using the energy produced when an organic material is oxidized by bacteria. The heterotrophic denitrifying bacteria require an organic carbon source, e.g., methanol, acetic acid, etc., as electron donor. Since such a heterotrophic denitrification process requires a large amount of organic materials, it has been utilized limitedly in treatment of wastewater rich in organic materials or organic materials have been added to the wastewater.

The present invention relates to an autotrophic denitrification process using sulfur as electron donor and requiring no addition of organic materials. The sulfur-using denitrifying bacteria oxidize sulfur to sulfuric acid and reduce nitrate to nitrogen gas, without requiring an organic material. And, the autotrophic denitrification using sulfur is economical because no carbon source is required and the amount of sludge generation is small. Accordingly, the sulfur-using denitrification process can be applied to treat groundwater, household sewage, contaminated surface water, toilet sewage, nitrified leachate and industrial wastewaters from chemical fertilizer industry, gunpowder industry, cell industry, petrochemical industry, nuclear power plant, etc.

The porous medium for denitrification using sulfur of the present invention may also be used to treat sewage and wastewater containing nitrate nitrogen through adequate control of the proportion of the components. But, preferably, it is used for treatment of groundwater, leachate, and so forth containing low-concentration nitrate nitrogen.

The powdered sulfur used in the present invention may be commercially available particulate sulfur or powdered sulfur. But, considering the cost, it is preferred to use elemental sulfur (powdered sulfur) obtainable from refineries as byproduct.

The addition of rock wool results in increased surface area and, thereby, makes bacteria attach and grow on the surface of the medium more easily. In general, rock wool has high moisture content and porosity. Preferably, the rock wool used in the present invention is obtained from agricultural waste and used after pulverizing, considering economical and environmental factors. Because conventional media comprising sulfur only or sulfur and $CaCO_3$ have smooth and hydrophobic surfaces (see FIGS. 3a and 3b), a long time was required for bacteria to attach and grow on sulfur particles. In contrast, the porous medium of the present invention which is prepared from sulfur, $CaCO_3$ and rock wool has increased specific surface area (see FIG. 3c), and is capable of increasing bacteria's sulfur utilization rate, or denitrification rate.

Stoichiometrically and empirically, a preferred mass ratio of the constituents of the porous medium of the present invention, that is the mass ratio of powdered sulfur : alkalinity agent : rock wool : nutrients is 9 : 9 : 1 : 1. But, in order to flexibly respond to alkalinity and nitrate nitrogen concentration of groundwater or leachate, the mass ratio of powdered sulfur : alkalinity agent : rock wool : nutrients is determined in the range from 8 : 8 : 1 : 1 to 10 : 10 : 1 : 1.

Preferably, in the porous medium of the present invention, the alkalinity agent is limestone ($CaCO_3$) or mollusk shells. The alkalinity agent is added to restore the alkalinity which is decreased by the denitrification using sulfur. For the alkalinity agent, limestone ($CaCO_3$), mollusk shells (clamshells, oyster shells, etc.), and the like that can be obtained inexpensively may be used. The alkalinity agent serves as inorganic

carbon source and pH buffer for the bacteria that attach to the sulfur medium and perform denitrification. Preferably, for easier mixing with the powdered sulfur, limestone, mollusk shells, etc. are used after pulverizing or one in powdered form is purchased for use.

Preferably, in the porous medium of the present invention, the nutrients comprise KH_2PO_4, $NaHCO_3$, $MgCl_2$ and $FeSO_4$. And, for the growth of the denitrifying bacteria the mass ratio of KH_2PO_4 : $NaHCO_3$: $MgCl_2$: $FeSO_4$ is preferably in the range from 10 : 4 : 2 : 1 to 12 : 6 : 4 : 1. More preferably, the mass ratio of KH_2PO_4 : $NaHCO_3$: $MgCl_2$: $FeSO_4$ = 11 : 5 : 3 : 1.

In another embodiment, the present invention provides a method for preparing a porous medium for autotrophic denitrification using sulfur (FIG. 1) comprising the steps of:

a) adding alkalinity agent selected from limestone and mollusk shells to powdered sulfur, adding pulverized rock wool and nutrients needed for the growth of denitrifying bacteria, and mixing well the same;

b) heating the resultant mixture to 130-150 °C, and mixing well to obtain homogeneous slurry; and

c) slowly cooling the resultant slurry with cold water, and pulverizing the same to obtain spherical media with size 2-5 mm.

【Mode for Invention】

The following examples illustrate the present invention and not intended to limit the same.

Example 1: Preparation of porous sulfur medium comprising powdered sulfur,

limestone ($CaCO_3$), rock wool and nutrients

Pulverized alkalinity such as limestone, mollusk shells, etc. is added to powdered sulfur. Then, finely pulverized rock wool and nutrients needed for the growth of denitrifying bacteria (see Table 1) are added and mixed well. Here, the proportion of the constituents is determined to be powdered sulfur : limestone : nutrients : rock wool = 9 : 9 : 1 : 1 (mass ratio). Then, the mixture is heated to 130-150 °C, so that other constituents are mixed with molten sulfur to form homogeneous slurry. The slurry is cooled slowly with cold water, pulverized using a mixer, and screened with a sieve (18-20 mesh) to obtain spherical media with size 2-5 mm (see FIG. 1).

FIG. 2 schematically illustrates the improved porous medium according to the present invention, which comprises powdered sulfur, $CaCO_3$, rock wool and nutrients. A biofilm is formed on the medium by the denitrifying bacteria attached thereto. Inside the medium, the nutrients needed for the growth of the denitrifying bacteria (not shown in the figure) are included.

[Table 1]

Composition of nutrients used in porous medium of the present invention

	Mass ratio (%)	Mass ratio based on mass of medium (%)
KH_2PO_4	55	2.75
$NaHCO_3$	25	1.25
$MgCl_2$	15	0.75
$FeSO_4$	5	0.25

Comparative Example 1: Preparation of medium comprising sulfur only

Powdered sulfur is heated to 130-150 °C. The molten sulfur is cooled slowly

with cold water, pulverized using a mixer, and screened with a sieve (18-20 mesh) to obtain spherical sulfur media with size 2-5 mm.

Comparative Example 2: Preparation of medium comprising sulfur and limestone only

Pulverized limestone is added to powdered sulfur. The proportion of the constituents is determined to be powdered sulfur : limestone = 1 : 1 (mass ratio). Then, the mixture is heated to 130-150 °C, so that limestone is mixed with molten sulfur to form homogeneous slurry. The slurry is cooled slowly with cold water, pulverized using a mixer, and screened with a sieve (18-20 mesh) to obtain spherical media with size 2-5 mm.

Example 2: Surface analysis of porous sulfur medium by SEM

The surface of the improved porous medium according to the present invention (Example 1) was compared with the medium comprising sulfur only (Comparative Example 1) and the medium comprising sulfur and $CaCO_3$ only (Comparative Example 2) by scanning electron microscopy (SEM) at 1000 X magnification (FIGS. 3a, 3b and 3c). As can be seen from the figures, the improved porous medium according to the present invention had a rougher surface, and hence larger specific surface area.

【Industrial Applicability】

As described, the porous medium of the present invention has increased specific surface area, thereby reducing the time required for denitrifying bacteria using sulfur to attach and grow on the surface of the medium. Further, it provides stable provision of alkalinity and supply of inorganic carbon source and nutrients needed by bacteria. Hence, the porous medium of the present invention can be effectively utilized for

treatment of groundwater containing nitrate nitrogen.

The present invention has been described in detail with reference to preferred embodiments thereof. However, it will be appreciated by those skilled in the art that changes may be made in these embodiments without departing from the principles and spirit of the invention, the scope of which is defined in the appended claims and their equivalents.

【CLAIMS】

【Claim 1】

A porous medium for autotrophic denitrification using sulfur for water treatment, which comprises powdered sulfur, alkalinity agent, pulverized rock wool and nutrients needed for the growth of denitrifying bacteria.

【Claim 2】

The porous medium according to claim 1, wherein the mass ratio of powdered sulfur : alkalinity agent : rock wool : nutrients ranges from 8 : 8 : 1 : 1 to 10 : 10 : 1 : 1.

【Claim 3】

The porous medium according to claim 1, wherein the alkalinity agent is limestone ($CaCO_3$) or mollusk shells.

【Claim 4】

The porous medium according to claim 1, wherein the nutrients comprise KH_2PO_4, $NaHCO_3$, $MgCl_2$ and $FeSO_4$.

【Claim 5】

The porous medium according to claim 4, wherein the mass ratio of KH_2PO_4 : $NaHCO_3$: $MgCl_2$: $FeSO_4$ ranges from 10 : 4 : 2 : 1 to 12 : 6 : 4 : 1.

【Claim 6】

A method for preparing a porous medium for autotrophic denitrification using sulfur comprising the steps of:

a) adding alkalinity agent selected from limestone and mollusk shells to powdered sulfur, adding pulverized rock wool and nutrients needed for the growth of denitrifying bacteria, and mixing well the same;

b) heating the resultant mixture to 130-150 °C, and mixing well to obtain homogeneous slurry; and

c) slowly cooling the resultant slurry with cold water, and pulverizing the same to obtain spherical media with size 2-5 mm.

DATED THIS 26TH DAY OF FEBRUARY 2008

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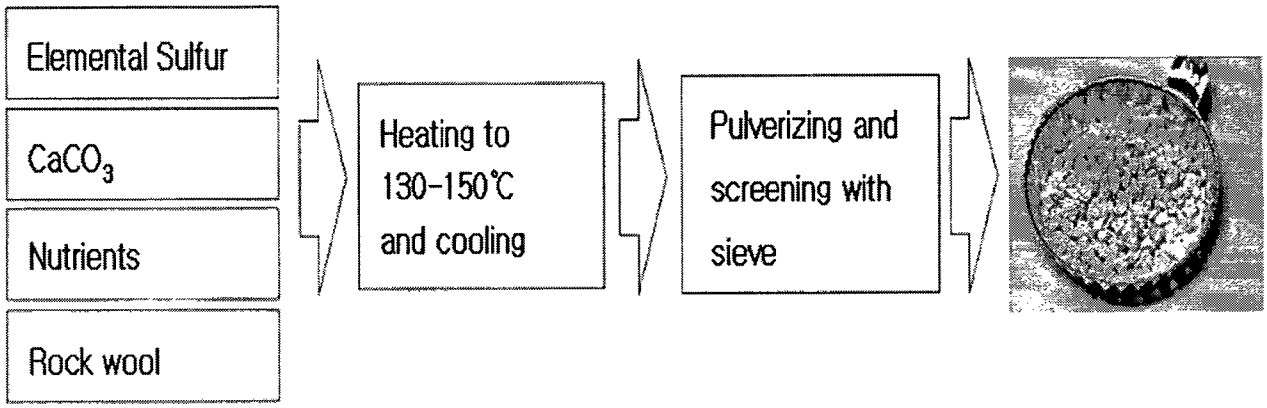
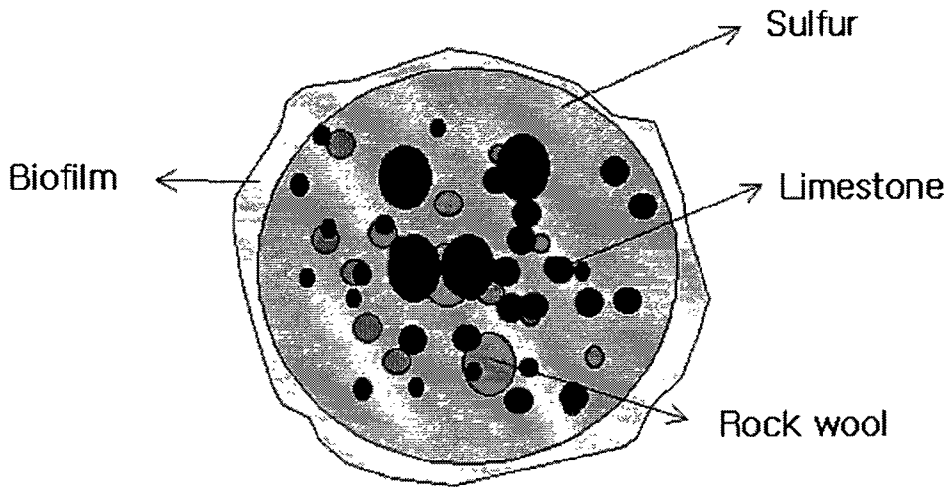
【FIG. 1】



【FIG. 2】



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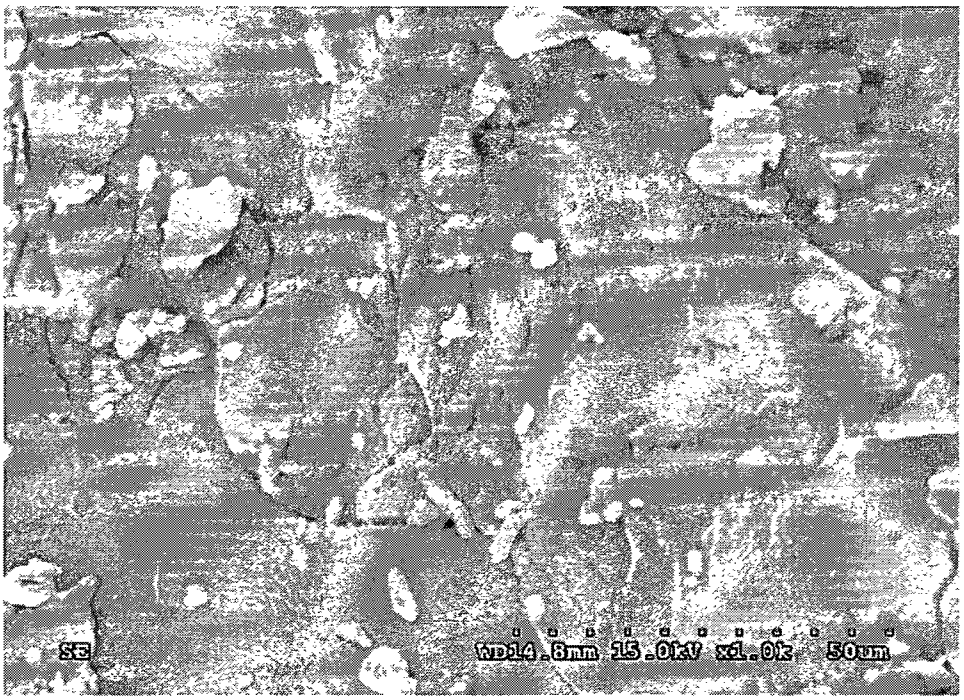
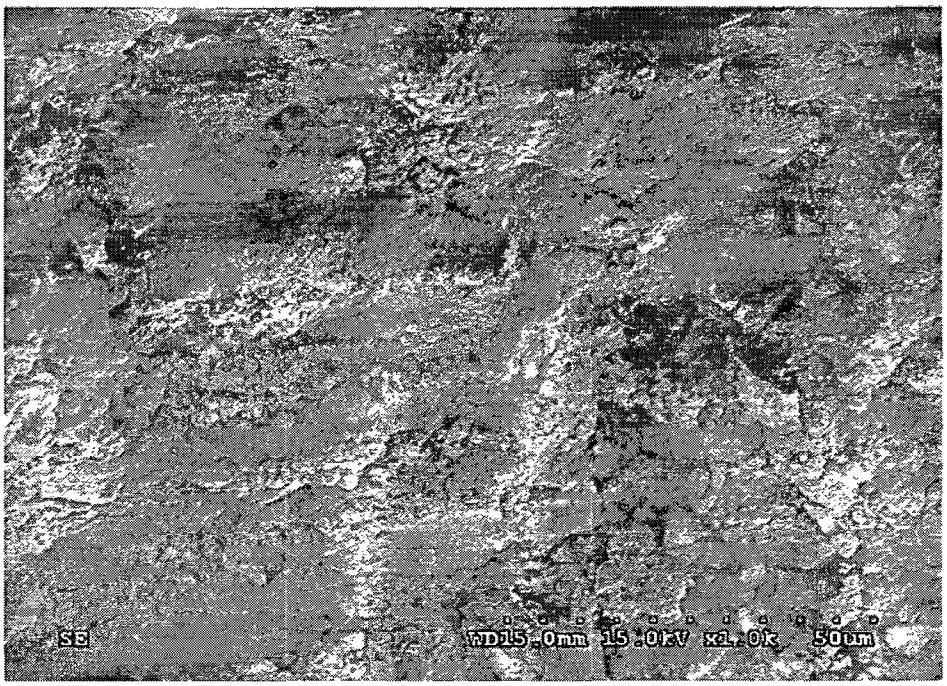
【FIG. 3a】



【FIG. 3b】



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【FIG. 3c】

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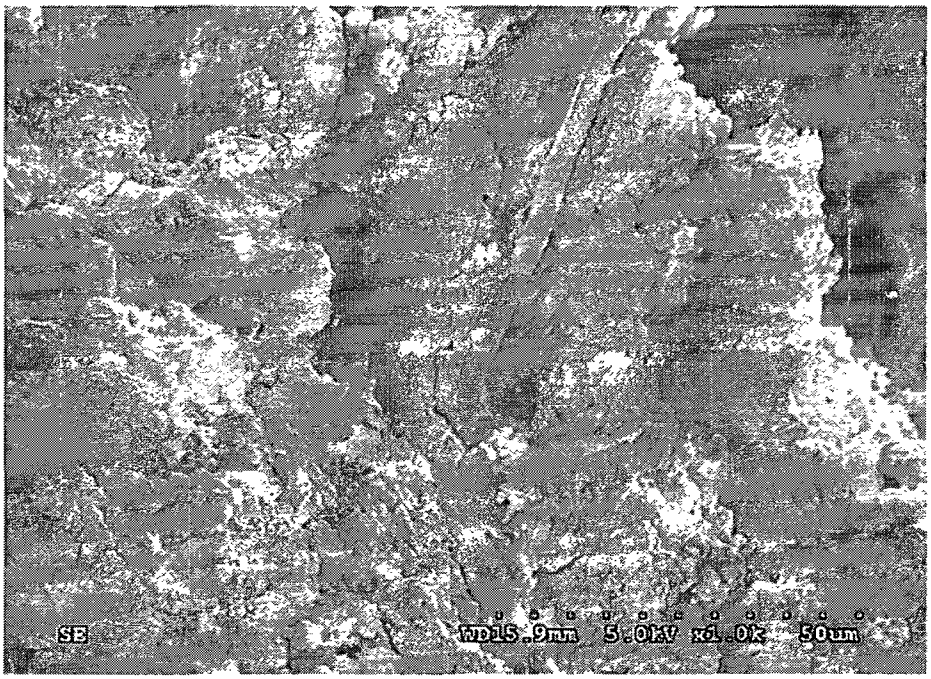

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