(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 December 2008 (24.12.2008)

PCT

(10) International Publication Number
WO 2008/154766 A2

(51) International Patent Classification: Not classified

(21) International Application Number:
PCT/CH2008/000278

(22) International Filing Date: 20 June 2008 (20.06.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1-2007-01230 20 June 2007 (20.06.2007) VN

(71) Applicants *(for all designated States except US)*: **BIBUS AG** [CH/CH]; Allmendstrasse 26, CH-8320 Fehraltdorf (CH). **HCTH TECNOLOGY INC.** [VN/VN]; km 2, Duong 196, Xa Nhan Hoa, Huyen My Hoa, Tinh Hung Yen (VN).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **TRAN, Con Hong** [VN/VN]; No.7, B2,TT DHTH, 51 Cam Hoi St., Dong Mac, Hai Ba Trung Dist., Hanoi (VN).

(74) Agent: **FREI PATENTANWALTSBÜRO AG**; Postfach 1771, CH-8032 Zürich (CH).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report*

WO 2008/154766 A2

(54) **Title:** METHOD OF PRODUCING AND RECYCLING ARSENIC ADSORBING MATERIALS FROM LATERITE

(57) **Abstract:** The invention proposes a method of producing a laterite based adsorption material for removing arsenic from drinking water. The laterite is heated for denaturation and than surface - activated to improve the adsorption capacity of the material. The adsorption material can be recycled many times in a recycling method and arsenic is collected in the form of calcium arsenate salt. The method of production of the laterite based adsorption material includes the following steps: calcinating laterite for denaturating at a temperature of 900 - 950°C, grinding and sizing the grains, soaking the grains in acid, neutralizing by NaOH, washing out soluble ions, drying and collecting the surface-activated laterite grains as arsenic adsorption material.

METHOD OF PRODUCING AND RECYCLING ARSENIC ADSORBING MATERIALS FROM LATERITE

FIELD OF THE INVENTION

The invention refers to a method of denaturating laterite by calcination and activation of the denaturated laterite surface to make it an adsorbant in order to eliminate arsenic from drinking water.

BACKGROUND OF THE INVENTION

It is known that the Bangladesh use clay which is heated to become terracotta (brick), ground and mixed with sand to filter arsenic containing water to make it drinking water. This treatment method is not very effective, because after heating the adsorbability of the clay is reduced significantly and it is not safe to discharge used materials.

In Vietnam up to now there have been no similar technologies announced and used in reality.

DESCRIPTION OF THE INVENTION

The purpose of the invention is to create a kind of material from natural laterite which has high arsenic adsorption capacity and can be recycled and does not pollute the environment. To reach the mentioned purpose, the invention uses laterite with a high iron content instead of clay. After calcinating for denaturation, the material surface is activated to enable the material to have high adsorption capacity for arsenic. The method includes the following steps: exploiting, calcinating for denaturation of laterite, grinding, classifying grains, activating the surface. The activated laterite after saturation by arsenic adsorption will be washed, recycled and arsenic is collected as calcium arsenate.

To perform the invention, the laterite used should normally have an iron content of 25-35%, with the rest being clay and other components. Laterite, after exploitation is naturally dried and then calcinated at the temperature of 900 to 950°C for 4 hours. Then it is cooled, ground and classified according to grain size and activated.

The activation process is performed as follows:

Step 1: Laterite grains are soaked in 1.0 N acid within 30 minutes; then the soaking solution is discharged.

Step 2: The material grains are continuously soaked in basic solution of 0.5 M NaOH within 30 minutes and then the solution is discharged.

Step 3. Using deionized water to wash out alkali and soluble ions and to obtain a neutral pH.

According to a preferred embodiment of the invention, hydrochloric acid is used and the iron (III) concentration is controlled to an optimal range before neutralization by the NaOH solution. This will give the best effects.

The laterite grain material after activation and drying will be used to load into columns like water filtering columns. The filtering columns can eliminate arsenic from drinking water to below 0.01 mg/l.

The laterite grain material after fully adsorbing arsenic will be recycled by washing with 0.2 M NaOH solution. The arsenic in the washing solution will be precipitated by $Ca(OH)_2$. Insoluble calcium arsenate is collected and the NaOH washing solution is recovered.

EXAMPLE OF AN IMPLEMENTATION OF THE INVENTION

68.5 kg of laterite exploited in Thach That (Ha Tay), after naturally drying it yields 50 kg of dry laterite. Such 50 kg of dry laterite is calcinated in electric ovens for 4 hours at a temperature of 950 ± 10 °C. Then it is naturally cooled for 24 hours and ground by hammer grinding machines which have screens with 4 mm holes. Grains below 1 mm in size are eliminated and dust is washed out and a yield of 27.5 kg denatured laterite grains sized from 1 to 4 mm is collected. 25 kg of denatured laterite grains are soaked in 20 1iters of 1.0 M HCl. After 30 minutes, the iron concentration is checked. When it reaches the optimal value, the acid solution is discharged. Next the laterite grains are soaked in 20 1 of 0.5 M NaOH solution for 30 minutes, then all the NaOH solution is discharged and the laterite grains are washed with clean water without arsenic until a neutral reaction is measured. The grains are dried and 24.85 kg of the activated laterite grain material is collected. This is used for treating water in order to remove arsenic and obtain drinking water.

EFFECTS OF THE METHOD ACCORDING TO THE INVENTION

By replacing clay with laterite and activation of the laterite surface after thermal denaturation, the method of this invention can adsorb arsenic stronger than heat

denatured clay: 1 kg of heat denatured clay adsorbs about 0.65 g arsenic whereas 1 kg of activated laterite grains can adsorb more than 6.00 g arsenic per kg of the material at the maximum. Furthermore, activated laterite can be recycled which reproduces activated surfaces to collect arsenate many times, whereas heat denatured clay cannot be recycled.

PATENT CLAIMS

1. A method of producing arsenic adsorption material based on laterite for water treatment comprising the following steps:

a) exploiting laterite, drying it , calcinating it for denaturation, and grinding it to yield grains

b) soaking the grains in an acidic solution to activate the grain surface

c) neutralizing the soaked grains, washing them for removing salts and drying them.

2. The method according to claim 1, wherein in step b) a concentration of iron (III) ions in the acidic solution is controlled in order to optimize the binding capacity of the laterite grains.

3. The method according to claim 2, wherein the soaking time in the acidic solution is adjusted such that a predetermined iron (III) concentration is reached.

4. The method according to anyone of claims 1 - 3, wherein the calcination of step a) is at a temperature of 900 - 950°C and lasts for 4 hours.

5. The method according to anyone of claims 1 - 4, wherein the acidic solution used in step b) is HCl and the neutralizing in step c) is performed with NaOH.

6. A method for recycling laterite-based arsenic adsorption material for water treatment comprising a washing step with a basic washing solution in order to release the adsorbed arsenate from the laterite grains into the basic washing solution.

7. The recycling method according to claim 6, which further comprises a step treating the basic washing solution for precipitating the released arsenate in form of an insoluble arsenate salt.

8. The recycling method according to claim 6 or 7, wherein the basic washing solution comprises NaOH.

9. The recycling method according claims 7 or 8, wherein Ca(OH)2 is used for precipitating the arsenate.