



Title	SIMULTANEOUS REMOVAL OF AMMONIA AND ORGANIC MATTERS FROM GROUND WATER BY COMBINATION OF ADSORPTION AND BIOLOGICAL TREATMENT PREPARATION OF BIOPOROUS ACTIVATED CARBON FROM RICE HUSKS AND ITS CHARACTERIZATION
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**SIMULTANEOUS REMOVAL OF AMMONIA AND ORGANIC MATTERS FROM GROUND
WATER BY COMBINATION OF ADSORPTION AND BIOLOGICAL TREATMENT**
PREPARATION OF BIOPOROUS ACTIVATED CARBON FROM RICE HUSKS
AND ITS CHARATERIZATION

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Abstract:

Both ground and surface water sources used for drinking purposes in rural regions are often contaminated with organics and ammonia originated from nature, agricultural and daily life activities.

The most popular and effective method for removing organic matters from aqueous media is the adsorption onto activated carbon. This method could be difficult to expand for rural areas in Vietnam due to high cost of activated carbon and the lack of regeneration equipment of exhausted carbon. Searching an inexpensive activated carbon and in some extent easy regeneration (for example, by biological mean) should be a good condition for organic removal in drinking water purification in rural areas.

Activated carbon from rice husks resource should be an appropriate solution for the purpose.

The paper presents some results on activated carbon preparation from rice hulls and the characterization of products obtained.

Many ground water resources using for drinking purpose in rural region are heavily contaminated with ammonia and organic matters. To remove these constituents, a schema is proposed in which the combination of adsorption onto activated carbon and the biological fixed film nitrification – denitrification process to be carried out.

To develop the technology, it requires a solid suited both as adsorbent and support media for fixing micro – organism. Activated carbon of macrospore structure is chosen for the purpose.

The preparation of low cost activated carbon from rice husks and the characterization of the products are the subject in this paper.

1. Present status of water supply in rural regions.

Mostly, the farmer families settle in small villages, subsisting on farming and rearing farm animals. Like the industrialized countries, community water supply systems were first provided for the large cities. Small cities and towns followed. In rural areas, community water supplies have been installed much late since public health considerations were less pressing than in urban although the people living here contribute to about 80% of the total population.

Since years, with the effort of government, the contribution of people living in rural regions and the aid of several international organizations, many small water stations were installed for providing drinking water to consumers.

The water supply by community stations does not cover all population living there because of limitation of funds and diffuse population distribution. Therefore many villages and families use the water resources locally available: canals, rivers, raining water and wells.

The water quality from different resources is poor, mostly does not meet the requirement for drinking purposes. Surface water is contaminated by organic matters and biologically not safe. Ground water contains high ammonia concentration and some heavy metals.

Some criteria of ground water being used for drinking purpose in Ha Nam province is presented in the table 1.

Table 1. Ground water characteristics (casual sampling in Ha Nam province at 11. 2001)

Number	Alkalinity (mg CaCO ₃ /l)	Hardness (mgCaCO ₃ /l)	NH ₄ ⁺ (mg/l)	Oxidability (mg O ₂ /l)	Fe (mg/l)	Arsenic (μ g/l)
1	420	201	23.0	14.2	12.0	24
2	122	1920	92.7	94.2	22.8	25
3	176	1840	65.9	88.6	10.8	26
4	614	400	29.0	15.8	2.5	31
5	612	344	41.5	49.4	11.0	36
6	168	100	9.3	5.0	8.0	89
7	338	270	40.0	19.5	5.6	78
8	556	392	48.4	7.5	4.0	168
9	586	195	77.6	17.1	18.3	569
10	414	330	19.1	4.8	7.0	263
11	296	720	85.3	39.5	28.5	733
12	702	460	119.4	41.4	26.0	237
13	340	227	84.5	56.4	17.8	204
14	380	530	60.5	54.1	14.5	203
15	366	688	94.7	55.4	15.0	226
16	390	616	78.9	54.8	21.8	237

These data show that the water quality is inadequate for drinking purpose with regard to organic matters and ammonia; they are harmful to the health of consumers.

Improving the water quality is therefore the urgency for the protection of public health.

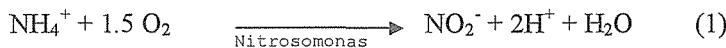
The prevailing treatment technology applied to the ground water is simple, consists of aeration, settling and sand filtration units. Such technology schema is ineffective to remove organic matters and ammonia.

2. Basis concepts and proposal solutions.

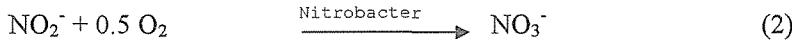
It was known, that adsorption is the dominant method for organic matter removal from water and nitrification – denitrification is the applicable procedure for ammonia removal.

Adsorption onto activated carbon is very effective in removing organic matter, especially the biological oxidation in fixed bed is involved [1, 2]. The most difficult step of activated carbon application is the regeneration of exhausted carbon, in particular, for small scale. On the other hand, the price of activated carbon is rather high in comparison to farmer's income.

Ammonia removal can be carried out biologically by oxidation (nitrification) in two steps:



Nitrite produced is, in turn oxidized by nitrobacter:



The nitrifiers need inorganic carbon (HCO₃⁻, CO₂) to multiply because of the heterotrophic character of the culture.

The reduction of nitrate, nitrite to nitrogen gas exists under anoxic conditions (nitrate plays the role of electron acceptor) and requires organic carbon resource which can be added or from the endogenous decay of bacterial cells.

Due to slow growth of nitrifiers, the nitrification process is often carried out by fixed film manner for increasing the mean cell residence time. An appropriate media for bacterial fixing is one factor for effective operation.

Many attempts were made to combine the adsorption onto activated carbon and biological filter to remove ammonia and organic compounds from water and wastewater simultaneously [3, 4]. The results obtained showed, the presence of powder carbon greatly improves both the nitrification and organic matter removal

efficiencies. Granular activated carbon bed can be also used for nitrification process (biological aerated filter) with high loading and high rate for ammonia removal [5, 6].

Denitrification process can be combined with the organic compounds adsorption process or using cell tissue for providing the needed carbon.

Activated carbon used in the whole process plays two roles: adsorbent for organic matter and bacterial fixing media. From the view point, that activated carbon having high surface area possesses narrow pore structure, and high adsorbility but unsuitable as fixing media used and vice versa. Therefore, a compromise between adsorption properties and biological activity of activated carbon has to be founded in respect of its porous structure. It can be expected, carbon of high porosity and of moderate surface area can be exploited for this purpose.

There is a large quantity of agricultural solid wastes: rice husk, peanut shell, coconut fiber, which can be used as raw materials for producing low cost adsorbents by simple anaerobic burning.

The low cost adsorbent can be utilized for organic matter removal alone or combined with biological aerated filter to achieve nitrification – denitrification process.

3. Activated carbon preparation from rice hulls and its characterizing.

Usually, activated carbon is produced from different carbonaceous materials by two steps: carbonization and activation, where in the first step the raw material is converted in carbonaceous form, the development of porosity and surface area is achieved in the second stage. The carbonization is often carried out under excluding of air (pyrolyse) to prevent the formation of carbon dioxide or carbon monoxide from raw materials. To develop the porosity one can use different agents and methods for activation: oxygen, carbon dioxide, water vapor or some acids and salts.

Rice hulls are the solid waste of agricultural production and it consists of organic material including some volatile compounds (acids, acetone, ketone, alcohols), silica and other inorganic substances (silica – cellulose structural arrangement) [7].

Chemical composition of rice husks is presented in table 1, 2.

Table 1. Chemical composition of rice husks [.....]

Constituent	Content range %
Moisture	2.4 – 11.4
Raw protein	1.7 – 7.4
Oil	0.4 – 3.0
Leachate without nitrogen	24.7 – 38.8
Fiber	31.7 – 49.9
Ash	13.2 – 29.0
Pentosane	16.9 – 22.0
Cellulose	34.3 – 43.8
Undissolve ash in acid	13.7 – 20.8

Table 2. Chemical composition of rice husks ash.

Constituent	Content range %
SiO ₂	86.9 – 97.3
K ₂ O	0.6 – 2.5
Na ₂ O	0.3 – 1.8
CaO	0.2 – 1.5
MgO	0.1 – 2.0
Fe ₂ O ₃	0.2 – 0.9
P ₂ O ₅	0.2 – 2.9
SO ₃	0.1 – 1.1
Cl ⁻	0.1 – 1.4

Rice husk possesses a large primary pore system and it will be extended in the pyrolysis process. Burnt rice husk presents a mixed adsorbent and may be used for organic and inorganic substances adsorption [7, 8].

Although the surface area of burnt rice husks will develop rapidly by increasing pyrolysis temperature, the value of surface area of products obtained is rather limited (up to 53 m²/g by 900°C pyrolysis temperature).

To improve the adsorbility of products, the activation can be applied either by physical or chemical method: activation by carbon dioxide, water vapor or by chemicals.

Silica is a major constituent of rice husks (table 1 and the activation process is conducted by the removal of silica from rice husks.

As known, sodium silicate is formed by reaction of silica (SiO₂) and alkaline reagents at high temperature and the product is easily dissolved in water.

Carbonization and chemical activation are combined in one step by the procedure: the rice husks are impregnated with sodium bicarbonate in the way so that the alkaline contents in the raw materials range from 0% to 30% by the weight. The pyrolysis process is performed in the temperature range 500 – 900°C and in the period 1 to 3 hours.

After pyrolysis, samples were leached with hot water until sodium silicate completely removed from burnt rice husks.

4. Characterization of products.

The products are characterized by true and apparent densities, porosity, BET surface area, iodine adsorption capacity (iodine number) and scanning electron microscope (SEM). The adsorbability is evaluated by adsorption of p-nitrophenole from aqueous solution.

True and apparent densities and the derived porosity of the carbonized product are determined by the method described in [1]. Surface area is obtained from nitrogen adsorption at – 196°C (Coulter SA 3100) (figure 1), the adsorption data were treated by BET – equation (software version 2. 13). Iodine number was determined by the method described in [9].

The adsorption isotherm data of p-nitro phenol are treated by Freundlcs equation:

$$A = K \cdot c^n$$

Where: a is the p- nitrophenole adsorbed onto carbon (mg/g), c is the concentration in aqueous phase (mg/l), K is the adsorption constant presenting the adsorption capacity at c = 1 mg/l. The adsorption capacity of different samples is compared through the K value.

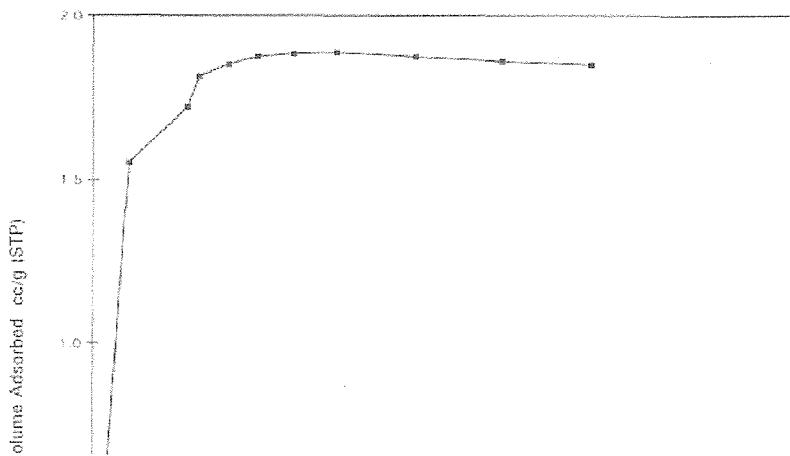


Figure 1. Nitrogen adsorption isotherm, sample burnt at 500°C

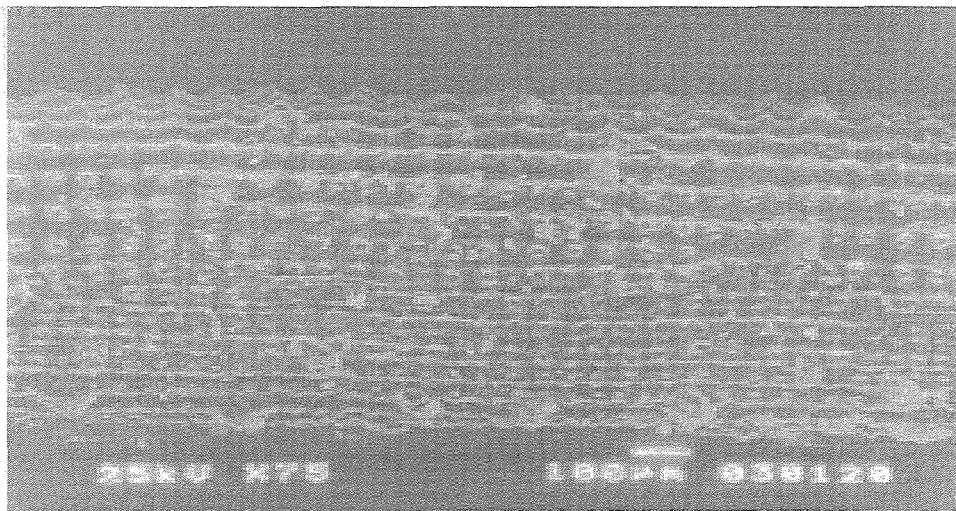


Figure 2. SEM picture of sample burnt at 500°C.

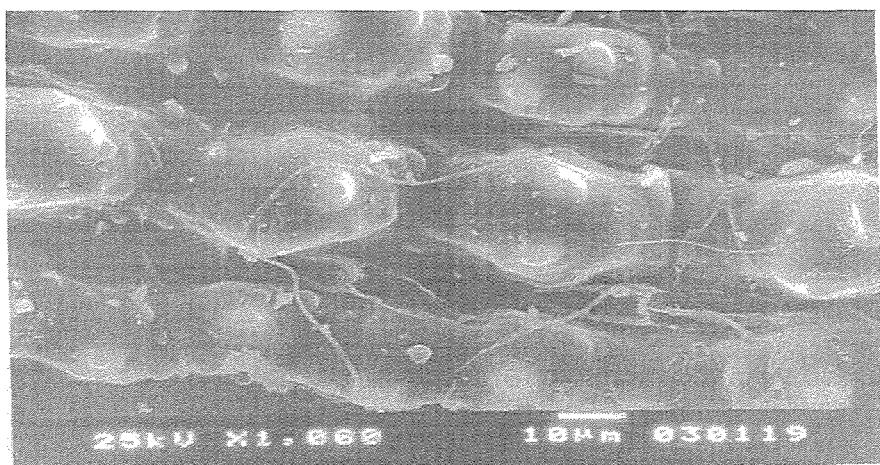


Figure 3. SEM picture of sample burnt at 460°C.

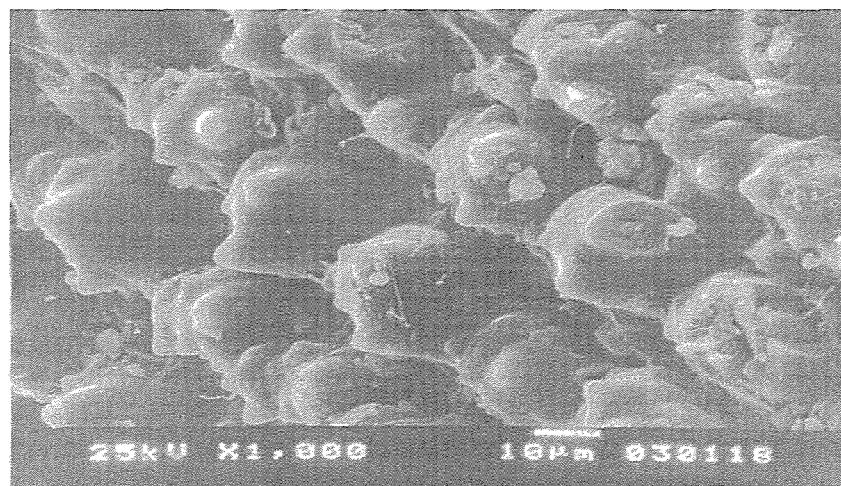


Figure 4. SEM picture of sample burnt at 500°C

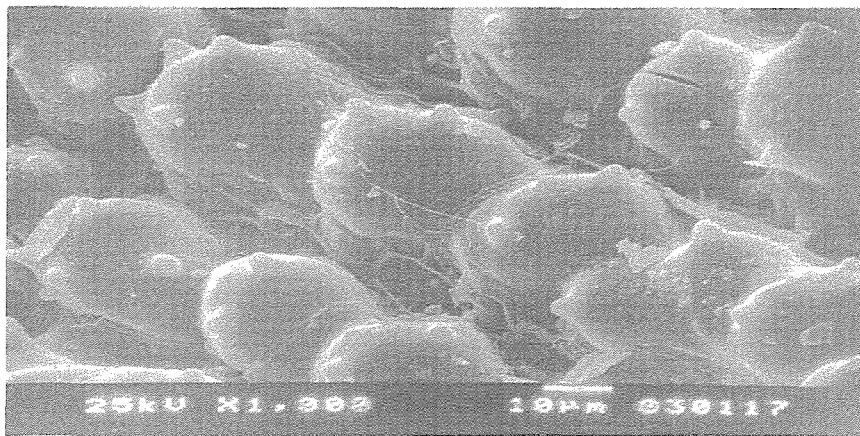


Figure 5. SEM picture of sample burnt at 340°C

Table 2. Activated carbon properties from rice husks at various burning temperatures.

Sample burnt at temperature, °C	258°C	340°C	362°C	460°C	500°C	900°C
Apparent density, g/cm ³	0.576	0.545	0.568	0.549	0.542	0.434
True density, g/cm ³	1.00	1.02	1.09	1.14	1.25	1.21
Pore volume, cm ³ /g	0.74	0.84	0.76	0.82	0.85	1.31
Porosity, %	43	47	48	52	57	61
Iodine number, mg/g	28	31	54	61	72	182
Surface area, m ² /g	-	7	-	-	53	359
Ash content, %	31.5	30.5	-	32.5	36.5	6.5

4. Results and discussion.

From table 2 we can see some typical features of the products obtained by varying burning temperatures: both surface area and porosity increase with increasing burning temperature.

At 900°C, the carbonized sample having a surface area of 359 m²/g was achieved, that is higher than the product activated by chemical method (ZnCl₂, at 750°C under nitrogen atmosphere, 2 – 3h) cited in [8].

Iodine number was considered as a measure of specific surface area of carbonaceous adsorbent, they are proportional together [1, 2]. At 900°C, the sample reached an iodine number of 180 mg/g.

The porosity also increases with temperature increasing but in a small extent.

Using the simple formula for the calculation of pore diameter:

$$d = \frac{5V}{S} \quad (3)$$

Where:

d: pore diameter in μm.

V: pore volume in cm³/g.

S: surface area in m²/g.

The pore size of different sample range from 0.018 to 0.6 μm. From SEM picture (figure 2, 3, 4, 5) we can see a regular pore system of the size about 10 μm and it varies not greatly from sample to sample burnt at various temperatures. From this fact we can speculate, that the adsorbent has a biporous structure: macro – micro pore system. This structure would have some advantages: micropore with large surface area would be utilized for organic constituents' adsorption and macropore system plays the role of the microorganism fixing sites.

5. Conclusion.

- * Many ground water resources in rural regions using for drinking purpose are heavily contaminated with ammonia and organic substances. They are harmful to the consumers.
- * One possible solution might be developed: preparation of low cost adsorbent from rice husks and other agricultural solid wastes by simple carbonization process. The obtained product is used as an adsorbent for organic matter adsorption and as a microorganism fixing media for nitrification – denitrification process.
- * Rice husk activated carbon was prepared by simple burning and characterized by different methods. The initial results show, that by varying burning temperature the products of different structures were obtained. The pore system seems to be a biporous structure and might be used both as an adsorbent and a fixing media for microorganism.

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