TREATING PHENOL IN WASTEWATER BY ACTIVATED CHARCOAL

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ABSTRACT

Phenols are generated in the wastewater of industrial processes. Phenol is extremely poisonous when entering the human body through the mouth. This study was conducted to determine the parameters of activated charcoal from coconut charcoal produced by Tam Dinh-Phu Yen Company and the ability of coconut charcoal in wastewater containing phenol. The results showed that the specific surface area was 891,7021 m^2/g and the surface area of the micropores was 848,3714 m^2/g. The moisture was less than 8 percent; the ash was from 2.38% to 4.7% and the particle size from 2.38% to 4.7% accounted for 97.2%. The highest emptiness at grain size was 1.25-2mm, accounting for 52.77 percent with a small surface area of 848.3714 m^2/g. The optimum efficiency of activated charcoal achieved best at pH = 5, the reaction time of 150 minutes, adsorption volume of 1-2.5 g; The processing efficiency was from 93.01% to 98.00% with the influent of 20-52mg/l.

Keywords: *Phenol, activated carbon, coconut shell, adsorption material*

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NGHIÊN CỨU XỬ LÝ PHENOL BẰNG THAN HOẠT TÍNH SỌ DỪA

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TÓM TẮT

Phenol phát sinh ra trong các dòng thải của quá trình công nghiệp. Phenol được xem là chất cực độc nếu đi vào cơ thể qua đường miệng. Nghiên cứu này thực hiện nhằm xác định các thông số của than hoạt tính sọ dừa được sản xuất bởi công ty Tam đỉnh Phú Yên và khả năng xử lý phenol trong nước của than sọ dừa. Kết quả cho thấy Diện tích bề mặt riêng là 891,7021 m^2/g, diện tích bề mặt riêng của lỗ nhỏ *(micropores)* là 848,3714 m^2/g m^2/g. Độ ẩm <8%, hàm lượng tro 0,8%, cỡ hạt chủ yếu của than từ 2,38 đến 4,7% chiếm 97,2%. Độ rỗng lớn nhất tại cỡ hạt 1,25-2 mm chiếm 52,77%. Với diện tích bề mặt riêng của lỗ nhỏ là 848,3714 m^2/g, khả năng xử lý phenol của than hoạt tính sọ dừa đạt tốt nhất ở pH = 5, thời gian phản ứng 150 phút, khối lượng vật liệu hấp phụ từ 1-2,5 g; hiệu suất xử lý đạt 93,01% đến 98,00% với phenol dòng vào từ 20-52 mg/l.

Từ khóa: *Phenol, than hoạt tính, sọ dừa, vật liệu hấp phụ.*

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1. Introduction

Activated carbon (AC) is a form of carbon that has been processed to form a porous structure to enhance the surface area of the coal. The surface area of ordinary coal is only tens of m^2/g coal, with activated carbon ranging from a few hundred to thousands of m^2/g [1] The adsorption and technical parameters of activated carbon are several times higher than that of conventional coal. Each type of coal with different production methods will have different compositions. In general, activated carbon is composed of 80-99.5% carbon, 0.3-3.3% hydrogen, 0.5-15% oxygen, 0.1-0.7% nitrogen and 0.1-0.7% sulfur [2]. Activated carbon is the material that has high carbon content but low inorganic components. It can be made of many different materials such as coal, bamboo, wood, coconut shells, peanut shell, corncob, rice husk and so on. Production methods create activated carbon of different properties, shapes and size. Activation increases the volume and widens the hole diameter. The hole structure and the distribution of the hole structure of coal are determined mainly from the initial materials and charcoal method [1]. Activation also removes non-structural carbon, exposes the crystals under the action of the activating agents and allows for the development of porous microstructure, the expansion of existing holes and the making of large holes by burning the bulkheads between adjacent holes. This causes the holes to move and the large holes increase, leading to a decrease in the volume of the hole.

According to Dubinin and Zaveria, activated carbon with a porous hole is created when the burning level is less than 50% and activated charcoal is formed when the burning level is greater than 75%. When the degree of combustion is between 50% and 75%, the product has a porous structure containing all types of holes. Activated carbon has a porous hole from one nm to several thousand nm [1]. Phenol (Carbolic Acid) is a compound of the formula: C_6H_5OH. The molecular weight of the phenol is 94.11 g/mol, the density is 1.06 g/cm^3. The melting temperature of the phenol is low, only 43°C so that in the phenolic medium the liquid exists. Phenol is a colorless or white substance while it is in pure form, where phenol is a crystalline solid. The odor threshold of phenol is 0.04 ppm [1]. At this concentration phenol has a sweet, spicy smell. In addition, phenol is very flammable and causes severe burns when exposed to the skin. The Ministry of Natural Resources and Environment of Vietnam has set the permissible limit of phenol in surface water less than 0.001mg/l due to its toxicity to the environment. Phenol can penetrate the human body through respiration and effects to the skin, eyes, mucous membranes of the body. Phenols are considered to be extremely poisonous if they enter the body through the mouth. Eating high phenolic content can lead to convulsions.

Treatment of activated carbon with activated carbon is considered an effective method to remove phenol from wastewater. Dhidan studied the use of activated carbon from rock to remove phenol in water by activating charcoal chemistry with iron chloride as an adsorber to remove phenol compounds. The result was a maximum of 98% phenol removal at pH=5 and a 90 minute exposure time [1]. Studies by Kadhim and Al-Seroury conducted the study of phenol removal in the column using rice shell adsorption [3]. Lua and Jia used activated charcoal palm oil to remove phenol. Studies show that phenol treatment efficiency for these materials is not high.

2. Experiment

2.1 Object and the scope of the study

Active coconut shell of Tam Dinh Company (Phu Yen province). The hypothetical environment contains phenols. The study was conducted on a laboratory scale.

2.2 Chemicals and research equipment

The chemicals used in the study include Hydrochloric acid (HCl), sodium thiosulfite solution ($Na_2S_2O_3.5H_2O$), standard iodine, potassium iodide (KI), basic standard iodate potassium (KIO_3) Sodium carbonate (Na_2CO_3), pure phenol (crystalline form), p.nitroaniline, sodium carbonate (Na_2CO_3), sodium nitrite ($NaNO_2$), sulfuric acid, distilled water.

Equipment and tools used in the research process at the laboratory of the Faculty of Civil and Environmental Engineering, the Laboratory of the Department of Materials Engineering of the Faculty of Materials Engineering - University of Industrial Technology and Laboratory of Physics - Medical University - Thai Nguyen University includes: - Analytical balance OHAUSPA 210, drying cabinet, electric stove, jar test 6-blade agitator, vibrating sieve, furnace, shaking machine HY - 5A, Molecular Absorption Spectrometer UV-VIS 02.

2.3 Analytical methods

- The standard method for checking the ash content of activated carbon - D2866-94

- The standard method for checking the moisture content of activated carbon - D2867-99

- The standard method for checking particle size distribution of activated carbon - D2862-97

- Determination of specific surface area, phenol in wastewater by BET measurement method and 64 TCN 102: 1997, respectively.

- Determining the isoelectric point of activated charcoal material

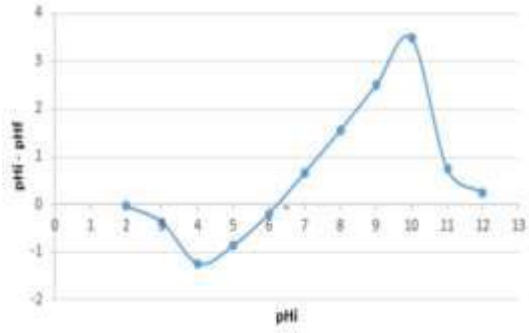

Figure 1. *Electrolyte of activated carbon from coconut shell*

3. Results and discussions

3.1 Evaluation of activated carbon from Coconut shell by Tam Dinh Company

3.1.1 Determining the specific surface area of activated carbon according to the BET method

The sample was sent to the Department of Chemistry - Department of Chemistry, Hanoi National University of Education and obtained results of the total surface area of coal being 891,7021 m^2/g, surface area of the micropores being 848,3714 m^2/g and the surface area being 43,3308 m^2/g. Compared with the results of research by Ali Gungogdu et al on the study of the surface area of active charcoal made from wood tea with a total surface area of 1066 m^2/g [4], coconut shell activated carbon had a smaller total surface area. However, that of activated carbon of coconut shell had a large area, accounting for 95.14% of the total surface area showed that it had the ability to adsorb molecularly having the small size.

3.1.2 Determination of moisture content of activated carbon

According to the standard method of checking the moisture of AC - D2867-99, activated charcoal made of coconut shell of Tam Dinh Company had a moisture of 7.41 percent with a particle size smaller than 0.3mm and 7.67 percent with a particle size greater than 0.3 mm.

Compared to the standard in the construction standard in Vietnam (TCVN 9069: 2012 - Granular filtering material for water purification - Test methods), the moisture content of activated carbon (pecentage of weight) was less than 8 percent. Thus coconut shell activated carbon had moisture within the allowable limits, met the requirements in the standard.

3.1.3 Determination of ash of activated carbon

According to the standard method of checking the ash content of activated charcoal D- 2866-94, charcoal made from coconut shell of Tam Dinh Company had percentage ash content of 2.51; 0.8; 0.79 respectively at 650^{o}C, 700^{o}C

and 750°C for 16 hours. At 700°C and 750°C, the ash content was negligible, so we chosen at 700°C to save the heat cost. Compared with the ash of activated charcoal produced by Tra Bac Company having 3 percent showed that the ash content of Tra Bac activated charcoal was 3.75 times higher than that of this research. Compared with the ash value of activated carbon produced by Coco AC company was 0.66%, the ash content of activated carbon produced by Tam Dinh company was not significantly higher with 0.13%.

3.1.4 Determination of the density of activated carbon

To determine the density of coal, the study was treated with particle size d> 5mm; 3-5mm; 2-3mm; 1.25-2mm; 0.15-1mm.

3.2 Research on phenol treatment

3.2.1 Effects of pH on the ability to process phenols

Based on the isoelectric point, about pH 2-6.2, the material surface is positively charged, so the pH range is 2-7; Puting in a conical volume of 100 ml phenol concentration 50 mg/l. Adjust pH with NaOH and H_2SO_4 to obtain a pH of 2-7; Adding to each 0.2g activated carbon had a particle size of 1-2mm; shaking for 150 minutes at a speed of 200 rpm and get results in Table 1.

Table 1 shows that at pH 5, treatment efficiency was highest, reaching 88.17% with adsorption capacity of 21.88 mg/g. Compared to the results of SS. Sreekumari et al., when studying the pH of phenol treatment by activated charcoal was 6, there is a difference with the result was optimal pH = 5 [5]. This difference may be due to the material being made from coconut shell and some other factors such as activation methods, equipments, laboratory instruments ... On the other hands, when compared with the results of Vinod and Anirudhan [6], pH of studying factors influencing phenol treatment by coconut shell activated charcoal respectively 5.5 and 5 shown similarity in research results. So pH = 5 was chosen as the optimum pH value.

Table 1. *Effects of pH on the ability to process phenols in water*

No	Mass of AC (g/l)	t (minutes)	pH	Co (mg/l)	Cr (mg/l)	H (%)	q (mg/g)
1	2	150	2.01	49.64	6.712	86.48	21.46
2	2	150	3.08	49.64	6.584	86.74	21.53
3	2	150	4	49.64	6.237	87.44	21.70
4	2	150	5.02	49.64	5.873	88.17	21.88
5	2	150	6.08	49.64	6.947	86.01	21.35
6	2	150	7.05	49.64	7.359	85.18	21.14

3.2.2 Effect of reaction time on phenol treatment

It was added to 7 conical flasks of 100 ml phenol concentration of 50 mg/l and adjusted pH to 5 with NaOH and H_2SO_4, then added 0.2g activated carbon to each flask with the size 1-2mm and shook for 150 minutes at a speed of 200 rpm. The survey period was 60 - 240 minutes and the results are shown in Table 2 and Figure 2.

Table 2. *Effect of reaction time on phenol treatment ability in the water environment*

No	Mass of AC (g/l)	t (minutes)	pH	Co (mg/l)	Cr (mg/l)	H (%)	q (mg/g)
1	2	60	5.08	54.71	15.84	71.05	19.44
2	2	90	5.08	54.71	12.54	77.08	21.09
3	2	120	5.08	54.71	9.953	81.81	22.38
4	2	150	5.08	54.71	5.894	89.23	24.41
5	2	180	5.08	54.71	5.835	89.33	24.44
6	2	210	5.08	54.71	4.365	92.02	25.17
7	2	240	5.08	54.71	3.718	93.20	25.50

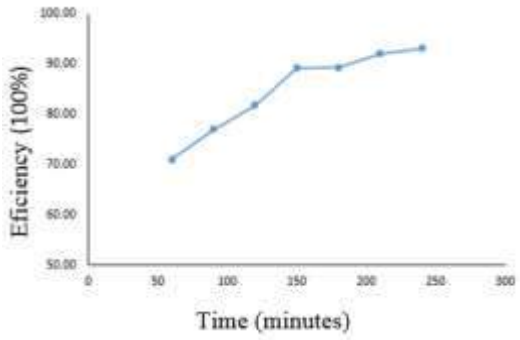

Figure 2. *Effect of reaction time on the phenol removal in water*

Table 2 and Figure 2 show that phenol treatment efficiency increased sharply from 60 to 150 minutes, from 71.05 to 89.23 percent. From 150 to 240 minutes, the processing efficiency reached 93.20 percent only increased by 3.97 percent. It can be assumed that at first time, the capillaries were not filled and the adsorption rate was high. Up to 150 minutes, the capillary was filled and the absorption area occupied large enough, so that the adsorption rate increased not significantly. Therefore, 150 minute was the optimal time. Compared to the study of Vinod V.P and Anirudhan T.S on the effect of time on phenol treatment influent with 50mg/l, pH 5.5, it can be shown that after 150 minutes of efficiency reached 72.6 percent, after 4 hours reached 94.4 percent [6]. Thus, the adsorption rate of activated charcoal was higher than that of activated charcoal in the study of Vinod V.P and Anirudhan T.S.

3.2.3 Effects of activated carbon content on phenol removal

100 ml phenol with the concentration of 50 mg/l was added into 7 conical flasks and it waw conducted to adjust pH to 5 with NaOH and H_2SO_4, then, added to each cone 0.1; 0.2; 0.25; 0.3; 0.35; 0.4; 0.5gram of activated carbon having particle size of 1-2mm. After shaking for 150 minutes at 200 rpm with a reaction time of 150 minutes, the results are shown in Table 3 and Figure 3.

Table 3. *Effect of AC Volume on Phenolic Treatment in Water*

No	Mass of AC (g/l)	t (minutes)	pH	Co (mg/l)	Cr (mg/l)	H (%)
1	1	150	5.06	52.35	15.42	70.54
2	2	150	5.06	52.35	5.69	89.13
3	2.5	150	5.06	52.35	3.66	93.01
4	3	150	5.06	52.35	2.07	96.05
5	3.5	150	5.06	52.35	1.42	97.29
6	4	150	5.06	52.35	0.682	98.70
7	5	150	5.06	52.35	0.638	98.78

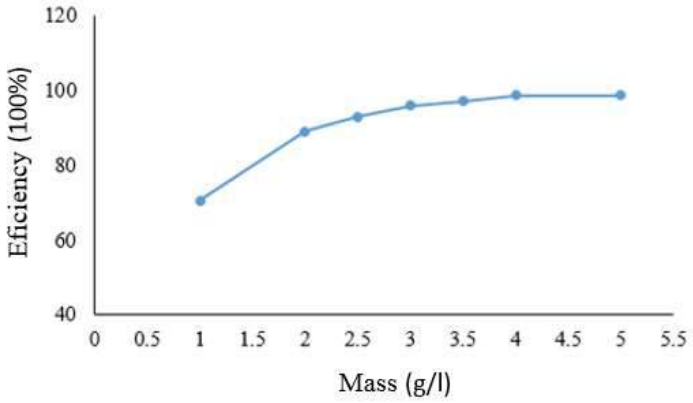

Figure 3. *Effect of AC Volume on Phenolic Feasibility in Water*

Table 3.4 and Figure 3.2 show that the treatment efficiency increased sharply from 1 to 2.5 g/l with a yield of 70.54 to 93.01 percent. In the range of 2.5-5g/l, the treatment efficiency increased

slowly. Compared with the studies of Anirudhan et al., at a concentration of 50mg/l, the reaction time was 4 hours, optimum coal volume was 2g/l with the treatment efficiency of 92.06% [6], which was higher than the Anirudhan's results 2.93% at the same volume. However, the retention time was 1.6 times. Therefore, 2.5g/l material is the optimal volume for the next survey.

3.2.4 Effect of Concentration on Phenol Treatment

Adding 10 cone volumes of 100 ml of phenol solution at 15; 20; 25; 30; 40; 45; 50; 55; 60 mg/l. Adjusting pH with NaOH and H_2SO_4; Adding to each 0.25g activated carbon size 1-2mm; Shaking for 150 minutes at a speed of 200 rpm. The results are shown in Table 4 and Figure 4.

Table 4. *Effects of phenol Concentrations on Phenolic Acid Treatment in Water*

No	Mass of AC (g/l)	t (minutes)	pH	Co (mg/l)	Cr (mg/l)	H (%)	q (mg/g)
1	2.5	150	5.05	16.24	0.332	97.96	6.36
2	2.5	150	5.01	20.94	0.419	98.00	8.21
3	2.5	150	5.02	24.32	0.681	97.20	9.46
4	2.5	150	5.00	31.24	1.614	94.83	11.85
5	2.5	150	5.04	36.21	2.17	94.01	13.62
6	2.5	150	5.03	39.11	2.441	93.76	14.67
7	2.5	150	5.00	46.02	2.915	93.67	17.24
8	2.5	150	5.06	52.35	3.66	93.01	19.48
9	2.5	150	5.01	56.82	4.894	91.39	20.77
10	2.5	150	5.00	58.4	5.66	90.31	21.10

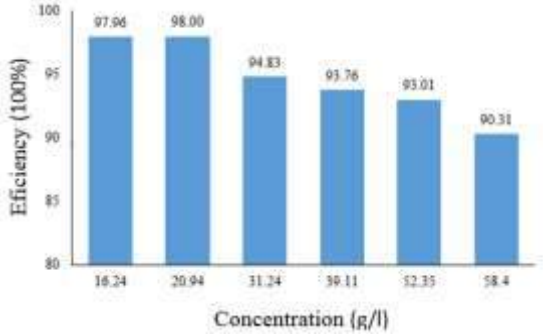

Figure 4. *Effect of phenol Concentrations on Phenolic Feasibility in Water Environment*

The results in Table 3.5 and Figure 3.3 show that at a concentration of 60 mg/l, the treatment efficiency was 90.31%. However, when the influent concentration was reduced to 20mg/l, the effluent concentration was 0.419mg/l and met the standards in column B of QCVN40: 2011/BTNMT - National Technical Regulation on industrial wastewater. This result was compared with that of Le Van Thuy and Vu Hoang Phuong [7] on the study of phenol in water by activated carbon from pine wood sawdust with coal weight of 3g/l, phenol concentration of 30mg/l, processing efficiency reached 81.1%. With the influent of 30mg/l, the volume of coal was 2.5g/l, the treatment efficiency of coconut shell activated charcoal produced by Tam Dinh company reached 94.83%. This suggests that coconut shell activated charcoal is better to handle phenol in water than the adsorbent in Thuy's study. Experimental results show that the activated carbon produced by Tam Dinh company is a good quality product, suitable for the treatment of phenol in water.

4. Conclusion

The study identified coconut charcoal produced by Tam Dinh Company as activated carbon with the following specifications: The surface area was 891.7021 m^2/g; the surface area of the micropores was 848.3714 m^2/g; moisture was less than 8 percent, ash content was 0.8 percent; The particle size of coal from 2.38 to 4.7 percent accounted for 97.2 percent. The highest emptiness at grain size was 1.25-2 mm, accounting for 52.77 percent. With a small surface area of 848.3714 m^2/g, coconut shell actived charcoal from Tam Dinh - Phu Yen Company has good

absorption capacity of small organic molecules. The study investigated a number of factors that affected the ability of phenol removal in the water of coconut shell activated charcoal produced by Tam Dinh Company and provided suitable conditions for adsorbing phenol pH = 5, reaction time being 150 minutes, adsorption volume of 2.5g/l, phenol concentration of 20mg/l, then treatment efficiency reached 98% and post-treatment phenol concentration met the standard Column B of QCVN 40: 2011/BTNMT National Technical Regulation on industrial wastewater.

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