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Production of Activated Carbon from Cocoa (*Theobroma cacao*) Pod Husk

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Abstract

Activated carbons were obtained from cocoa pod husk using two different initial particle sizes (ranges 0.25 – 0.50mm and 0.50 – 1.00mm), three chemical activation agents (K_2CO_3, KOH and $ZnCl_2$) and carbonization under nitrogen atmosphere during two hours at three different temperatures (500°C, 650°C and 800°C).

The prepared activated carbons were characterized using Brunauer–Emmett–Teller (BET) and Langmuir surface areas, pore volume, average pore size, bulk density, moisture, ash content, and yield. The five best activated carbons were selected for further experiments according to the chemical activation agent used, high BET surface area, high pore volume and low ash content. Additionally, content of impurities, carbon content and FE-SEM micrographs were determined for these five best activated carbons. As adsorption tests were also carried out with these samples.

Results of the experiments show that cocoa pod husk is a material that can be used to produce activated carbon by chemical activation and $ZnCl_2$ showed to be the best chemical activation agent based on the highest BET surface area (780 m^2/g in the best case) and pore volume (0.58 m^3/g in the best case), the lowest ash content (6.14% in the best case), and the highest carbon content (86.1% in the best case), compared with others chemicals. Carbons activated by $ZnCl_2$ are capable to adsorb As(V), getting As(V) removal levels up to 80% in less than 1 hour in the experimental conditions applied (initial pH 6-7, activated carbon concentration 0.1 g/l and 0.5 g/l, initial As concentration 100 ppb).

Keywords: Activated carbon; Cocoa pod husk; Chemical activation; Physical-chemical characterization; Adsorption

Introduction

Adsorption with activated carbon is a useful treatment method to remove pollutants from waters and wastewaters. However, commercial activated carbons are expensive and it is important to find out new low cost materials available for use as adsorbents. A wide range of studies have been conducted to reach this aim, using cocoa pod husk [1-3] and different agricultural and forest wastes as raw materials, e.g. macadia nutshell [4], rice husk [5-7], jatropa husk [8], wood apple shell [9], pine nutshell [10], oil palm shell [11], seed shell of the palm tree [12], sago waste [13], guava seed [14], almond shell, pistachio shell, walnut shell [15], olive mill waste [16] and others.

Besides economic implications, the use of agricultural byproducts has environmental advantages [17]. In Peru agricultural wastes as cocoa pod husk are disposed in unsuitable conditions, generating bad smell, microorganisms, pollution of water stream and considerable impacts on the landscape. Another advantage from the environmental point of view is that cocoa pod husk may be considered as a renewable resource because it has been replenished continuously.

Cocoa pod husk represents between 70 to 75 % of the whole weight of the cocoa fruit, i.e. per each ton of cocoa fruit there will be between 700 to 750 Kg of waste. Nevertheless, some alternatives have been carried out to avoid the final disposal as well as to create valuable products, e.g. food antioxidants [18], dietary fibers [19], animal feed [20]. Cocoa pod husk shows good features to be used as a precursor in the activated carbon production due to its cellulosic and hemicellulosic content [21].

Cellulosic, hemicellulosic and lignocellulosic materials may be activated using two groups of methods, physical activation and chemical activation. Physical activation involves the use of steam, air, CO_2 or a combination of those as an activation agent, while chemical activation uses reagents such as $ZnCl_2$ [7,8], H_3PO_4 [8], KOH [8,22], K_2S, KCNS or K_2CO_3 [5]. However, chemical activation shows several advantages when compared to physical activation. It uses lower temperatures than pyrolysis, it usually needs only one step, in general it leads to a much higher yield than the physical activation, it allows to obtain activated carbons with very high surface areas and well developed micro porosities, and there is an important reduction of the mineral matter content in the activated carbons obtained.

The adsorption of heavy metals from waters and wastewaters using activated carbon as the treatment method has been studied by several authors; Shukla and Sakhardanre [23] studied Hg and Pb adsorption, Orhan and Buyukgungor [24] Cd and Cr adsorption, Kumar and Bandyopadhyay [25] Cd and Hg adsorption, Jameel and Hussain [6] Pb, Cu, Ni and Cr adsorption, Tangjuank et al. [22] Pb(II) and Cd(II) adsorption, Khan et al. [7] Cu (II) adsorption, Cem et al. [26] Zn, Cu and Pb adsorption, among others.

Arsenic (As) is one of the pollutants that have several environmental and health implications. The main concern of arsenic is that it can be introduced in food chain e.g. via contaminated drinking water, causing several health effects especially cancer [27]. Arsenic has always been a problem in groundwater pollution; however, nowadays there is also an emerging problem in surface waters. For example in Tumbes River, Peru, arsenic has been found in levels much higher than Peruvian water quality standard allows [28]. Thus, it has become a severe problem since people in rural areas drink this water without any treatment.

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This study aims to produce a low-cost activated carbon from cocoa pod husk using three different chemical activation agents, three different carbonization temperatures and two different particle sizes of the raw material. The prepared adsorption materials were characterized by different surface science methods and their performance was compared by testing the preliminarily As adsorption capability of the five best activated carbons.

Material and Methods

Raw material

Cocoa pod husk samples were collected from four different areas in Tumbes, Peru. Based on Oladayo [21], the characteristics of cocoa pod husk are: moisture content 10.04±0.03 %, ash content 12.67±0.19 %, crude fiber content 33.60±0.15 %, hemi-cellulose content 35.26±0.05 %, lignin content 0.95±0.04 %, and cellulose content 41.92±0.09 %. In addition, the following compounds in cocoa pod husk have also been reported by Aregheore [20]: crude protein 6.2 %, ether extract 1.4 %, calcium 1.63 g/kg, phosphorus 0.17 g/kg, potassium 2.18 g/kg, sodium 0.36 g/kg , magnesium 0.24 g/kg, copper 135.2 mg/kg, manganese 45.6 mg/kg, and zinc 90.3 mg/kg.

Reagents

All the chemicals were of analytical reagent grade and used without further purification. The activation chemicals used were K_2CO_3, $ZnCl_2$ both purchased from Merck, and KOH purchased from Sigma-Aldrich. Sodium arsenate dibasic heptahydrate ($HAsNa_2O_4{\cdot}7H_2O$) from Sigma-Aldrich was used for preparing the 100 mg/l As stock solution for adsorption experiments. The stock solution was preserved with ultrapure concentrated (65 %) nitric acid (HNO_3) in order to have a final acid concentration of 0.2 % in the solution. De-ionized water from a Millipore Milli-Q water system was used for all dilutions of the stock solution.

Carbonization equipment

The equipment for the activation of cocoa pod husk is seen in Figure 1. The equipment contained a nitrogen supply, a nitrogen mass flow controller, a furnace, a tubular reactor, a ceramic container for the sample and a trap for gaseous compounds.

Production of activated carbon

Cocoa pod husk was dried at 80°C until a constant weight was obtained, ground and sieved to two fractions: 0.25 – 0.5 mm and 0.5 – 1 mm. K_2CO_3, KOH and $ZnCl_2$ were used as activation chemicals for raw material in a weight proportion 1/1. In the case of K_2CO_3 and KOH water was added to the samples in a weight proportion 1/1 (water/mix), dried at 100°C overnight and carbonized at different temperatures 500, 650 and 800°C. In the case of $ZnCl_2$ samples were carbonized directly without water addition and dried.

The heating rate of 10°C/min was applied to reach the carbonization temperature, in which the samples were kept for two hours and then cooled down to room temperature. The whole process of carbonization was done under nitrogen atmosphere (150 ml/min).

After carbonization, the samples activated with K_2CO_3 were washed with boiled distilled water and room temperature water. The samples activated with KOH and $ZnCl_2$ were washed with a dilute solution of HCl (0.5 N) and room temperature water. Finally, all samples were dried at 100°C overnight, ground and sieved on a mesh of 0.25 mm pore size. Table 1 presents the conditions during the activations and the names used for the activated carbons produced.

Characterization of activated carbon

Activated carbons obtained were characterized using BET surface area (m^2/g), Langmuir surface area (m^2/g), pore volume (m^3/g), average pore size (nm), moisture content (%), dry matter content (%), ash content (%), yield (%) and bulk density (kg/l) measurements.

Micromeritics ASAP 2020 Surface area and porosity analyzer was used to determine BET surface area, Langmuir surface area, pore volume and average pore size. The BET method was used to calculate the surface area, based on selected N_2 adsorption data within the p/p_0 range of 0.057–0.203. The total pore volume and the average pore size were derived using the BJH (Barret-Joyner-Halenda) method. Moisture was determined by a gravimetric method and ash content of the carbons was determined using the standard ASTM procedure D2866-94. The yield was calculated by the following equation

$$Yield(\%)=\frac{FW}{IW}\times 100\% \qquad (1)$$

where FW is the final weight after carbonization process and IW is the initial raw material weight used before the addition of a chemical activation agent.

The best five samples according to the chemical activation agent, surface area and ash content were selected to carry out deeper analysis such as carbon content (%), impurities content (mg/kg) and existence of impurities and surface uniformity (Fe-SEM images). Impurities were analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) Perkin Elmer Optical Emission Spectrometer Optima 5300 DV. The samples were first dissolved with a mixture of HNO_3, H_2O_2, HF and HCl in microwave oven before analysis with ICP-OES. Fe-SEM images were obtained using a Field Emission Scanning Electron Microscopy ZEISS ULTRA plus equipped with Oxford Instruments INCA-X-act EDS detector.

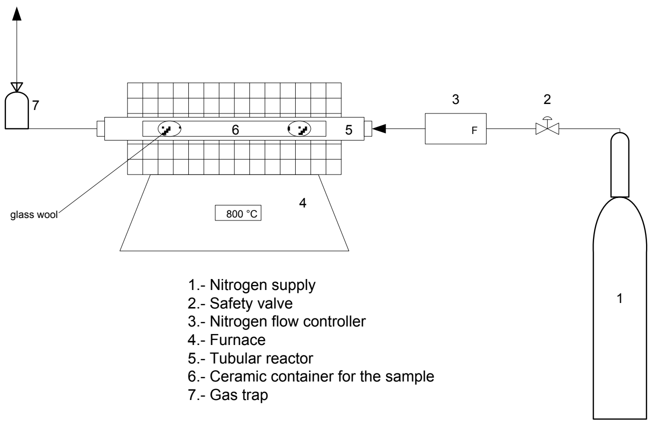

Figure 1: Carbonization equipment.

Carbonization Temperature (°C)	Chemical Activator					
	K_2CO_3		KOH		$ZnCl_2$	
	Particle size (mm)		Particle size (mm)		Particle size (mm)	
	0.25 – 0.5	0.5 – 1	0.25 – 0.5	0.5 – 1	0.25 – 0.5	0.5 – 1
500	CPH-18	CPH-15	CPH-10	CPH-12	CPH-24	CPH-21
650	CPH-16	CPH-17	CPH-08	CPH-11	CPH-22	CPH-23
800	CPH-13	CPH-14	CPH-07	CPH-09	CPH-20	CPH-19

Table 1: Description of conditions during the activation process.

Adsorption experiments

Batch adsorption experiments were carried out to test the arsenic adsorption capability of the five best activated carbons obtained. The experiments were conducted at room temperature. The initial arsenic concentration of 100 µg/l in the 200 ml batches was achieved by diluting the As stock solution with Milli-Q water. The initial pH of the arsenic solution was between 6 and 7 and the experiments were conducted without adjusting the solution pH during the test. The activated carbon loadings were 0.5 g/l and 1.0 g/l. The solutions were shaken with a mechanical shaker Certomat at 175 rpm for six hours. Samples were taken periodically at the initial time, 5, 15, 30, 60, 120, 180, and 240 minutes, filtered through 0.45 µm syringe filters and acidified with p.a. nitric acid in order to maintain the preservability of the samples. Arsenic concentration of the samples was analyzed using Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) Perkin Elmer A Analyst 600.

Results and Discussion

Characterization of activated carbons

The characterization results for activated carbons obtained are shown in Table 2. For the samples CPH-07, CPH-08 and CPH-10 it was not possible to obtain results because the yields were insignificant, due to the following reasons: cocoa pod husk particles between 0.25 – 0.5 mm were digested by KOH, high volatilization took place during the carbonization stage or/and the material losses during the washing stage were high because of very low particle size and water solubility of the material.

In the case of KOH the best results of surface area, pore volume and ash content were obtained at 800°C (the highest temperature applied). At 500°C and 650°C, high surface areas were not obtained. This tendency may be because the activation mechanism of KOH in order to generate high porosity needs high temperatures, i.e. temperatures around 800°C. Similar behavior was found by Ahmadpour [4] in the preparation of activated carbon from Macadia Nutshell.

The best results in the samples activated by K_2CO_3 were obtained at 800°C, and the results show that the quality of activated carbons improves with an increase in the carbonization temperature in the range between 500°C to 800°C. Hayashi et al. [15] found the same results working with various nutshells, however, this behavior changes at carbonization temperatures higher than 900°C.

In general, $ZnCl_2$ was apparently the most effective chemical agent to activate cocoa pod husk, obtaining for all temperatures and particle sizes (all the experiments) the highest BET surface area, highest pore volume and the lowest ash content. Samples prepared by $ZnCl_2$ at 500°C and 650°C showed the best results of surface area and pore volume, while samples prepared at 800°C had lower quality which may be a consequence of $ZnCl_2$ evaporation during carbonization [4].

$ZnCl_2$ activated carbons obtained the highest final yield, then K_2CO_3 activated carbons and finally KOH activated carbon. It is because of the difference between impregnation methods applied; impregnation in $ZnCl_2$ activation was only for minutes in dry conditions and at room temperature, while in K_2CO_3 and KOH the impregnation was in wet conditions and overnight at 100°C. Different reaction mechanisms in the activation are another cause for these yields. According to Ahmadpour [4] $ZnCl_2$ (a Lewis acid) promotes the aromatic condensation reactions, which produce an increase in the yield; while KOH (a strong base) catalyzes the oxidation reactions, which results in further carbon gasification. Reaction mechanism of K_2CO_3 at temperatures above 600°C involves its conversion into CO [15] and the significant loss in yield.

The five best activated carbons according to chemical activation agent, BET surface area, pore volume, and ash content were: CPH-09 (0.5-1 mm/KOH/800°C), CPH-13 (0.25-0.5 mm/K_2CO_3/800°C), CPH-14 (0.5-1 mm/K_2CO_3/800°C), CPH-21 (0.5-1 mm/$ZnCl_2$/500°C) and CPH-22 (0.25-0.5 mm/$ZnCl_2$/650°C), respectively. These criteria were chosen because these parameters are the most important parameters in the quality of activated carbons. The chemical impurities for contents for these five samples were analyzed with ICP-OES and are shown in Table 3.

The content of impurities was high in the samples analyzed; CPH-09, CPH-13 and CPH-14 have high K levels because of reagents KOH and K_2CO_3 used in the activation; CPH-21 and CPH-22 show high levels of Zn as impurity, also because of the chemical activation reagent $ZnCl_2$. It will be necessary to adjust the washing in order to reduce the amounts of these impurities [29,30]. Some of these impurities are originating from the natural composition of the cocoa pod husk.

The average carbon content in the samples was 72.9 % for CPH-

Sample Code	Temp. (°C)	Chemical activator	Particle size(*) (mm)	Final yield (%)	Bulk Density (Kg/l)	Ash (%)	Moisture (%)	Dry matter (%)	BET surface area (m^2/g)	Langmuir Surface Area (m^2/g)	Pore Volume (m^3/g)	Average Pore Size (nm)
CPH – 09	800	KOH	0.5 - 1	13.5	0.1	22.3	6.8	93.2	490	648	0.24	2.0
CPH – 11	650	KOH	0.5 – 1.0	20.7	0.23	53.0	9.0	91.0	8	10	0.02	7.9
CPH – 12	500	KOH	0.5 – 1.0	21.0	0.22	51.5	8.7	91.3	7	9	0.01	7.0
CPH – 13	800	K_2CO_3	0.25 – 0.5	24.2	0.12	20.5	6.9	93.1	615	811	0.31	2.0
CPH – 14	800	K_2CO_3	0.5 - 1	19.9	0.1	11.4	6.0	94.0	614	811	0.31	2.0
CPH – 15	500	K_2CO_3	0.5 - 1	28.5	0.21	20.2	6.8	93.3	8	12	0.01	5.2
CPH – 16	650	K_2CO_3	0.25 - 0.5	14.8	0.15	13.2	8.9	91.1	320	424	0.17	2.1
CPH – 17	650	K_2CO_3	0.5 - 1	31.3	0.15	17.7	7.0	93.0	8	12	0.02	7.3
CPH – 18	500	K_2CO_3	0.25 - 0.5	21.7	0.13	10.7	5.8	94.2	12	17	0.02	6.4
CPH – 19	800	$ZnCl_2$	0.5 - 1	36.6	0.41	8.8	4.3	95.7	562	771	0.42	3.0
CPH – 20	800	$ZnCl_2$	0.25 - 0.5	35.3	0.36	6.4	4.3	95.7	574	782	0.38	2.6
CPH – 21	500	$ZnCl_2$	0.5 - 1	42.5	0.28	6.1	3.3	96.7	724	993	0.53	2.9
CPH – 22	650	$ZnCl_2$	0.25 - 0.5	37.3	0.32	11.9	3.0	97.0	780	1064	0.58	2.9
CPH – 23	650	$ZnCl_2$	0.5 - 1	44.9	0.33	11.5	4.5	95.5	663	912	0.57	3.4
CPH – 24	500	$ZnCl_2$	0.25 - 0.5	47.2	0.32	12.8	4.4	95.6	599	817	0.43	2.9

(*)Particle size of the raw material

Table 2: Results of characterization of activated carbons obtained.

09, 76.6 % for CPH-13, 69.6 % for CPH-14, 86.0 % for CPH-21 and 82.9 % for CPH-22. Samples activated by $ZnCl_2$ have the highest carbon content, which is good for the quality of activated carbon in order to adsorb pollutants.

Fe-SEM micrographs in Figure 2 show the development of porosity of the five best samples. However, the structure and size of the pores vary according to the chemical activation agent. For the five best samples, the average pore size is low, because of the predominance of structure of micro pores. However, activated carbons activated by KOH and K_2CO_3 (2 nm in average, see Table 2) have pores smaller than activated carbons activated by $ZnCl_2$ (3 nm in average, see Table 2). Cocoa pod husk is a material with high content of cellulose and low content of lignin; this is the reason to get predominantly micro porous structure [31].

The pore size distribution of activated carbons activated by $ZnCl_2$, shows a well developed mesoporous structure. It is possible to find micropores inside of these mesopores. This is very important from the water treatment point of view, because mesoporous structure allows water or wastewater to penetrate into activated carbon and to get in contact with the micropores in order to permit the adsorption of heavy metals and pollutants of high molecular weight such as organic compounds.

Fe-SEM micrographs also show the impurities found with ICP-OES analysis including the presence of charged particles (bright ones) evolved from chemical activation agents.

Adsorption experiments

Redox potential and pH are the most important parameters in the heavy metal speciation in aqueous solutions. Values of pH between 6 – 7 and oxidizing conditions were chosen for the adsorption experiments because of river water conditions in the north of Peru, the place where the future adsorption experiments will be done. In these experimental conditions, the aqueous speciation of arsenic is dominated by As(V), and more specifically oxyanions $HAsO_4^{2-}$ and AsO_4^{3-} are the predominant aqueous forms [32].

Only the activated carbons activated with $ZnCl_2$ (CPH-21 and CPH-22) were capable to adsorb arsenic in the experimental conditions (initial pH 6-7, activated carbon concentration 0.5 g/l and 1.0 g/l, initial As concentration 100 ppb).

Regarding the prepared materials activated by K_2CO_3 and KOH, the problem was the increase of pH; both these activated carbons were basic and when they were added to the initial As solution the pH increased up to 8 or 9. The impurities content in the activated carbon is a negative factor for the adsorption of As(V), since the chemical activation agents are still remaining in the surface of the samples, which is the reason for the increase of pH. Since the surface charge of AC is presumably positive at lower pH values and negative at higher pHs, there may be repulsive forces at basic conditions between the negatively charged activated carbons and anionic As(V) species, and the adsorption does not occur. These ACs might work in adsorbing As at lower pH values.

Figure 3 shows that the rate of adsorption of As(V) is high at the initial state (between 0 – 50 minutes) then the rate decreases rapidly. According to Jameel and Hussain [6] this is due to adequate availability of active sites at the initial period.

As seen from Figure 3 the adsorption of arsenic with CPH-22 decreases remarkably from approximately 70 % to 30 % removal when the loading of the activated carbon is increased. Aggregation of adsorption sites might cause this behavior resulting in decrease in total adsorbent surface area available for As(V) adsorption and an increase in diffusion path length [33]. With CPH-21 the effect is not the same and the removal of arsenic stays at the same level with both the loadings of activated carbon.

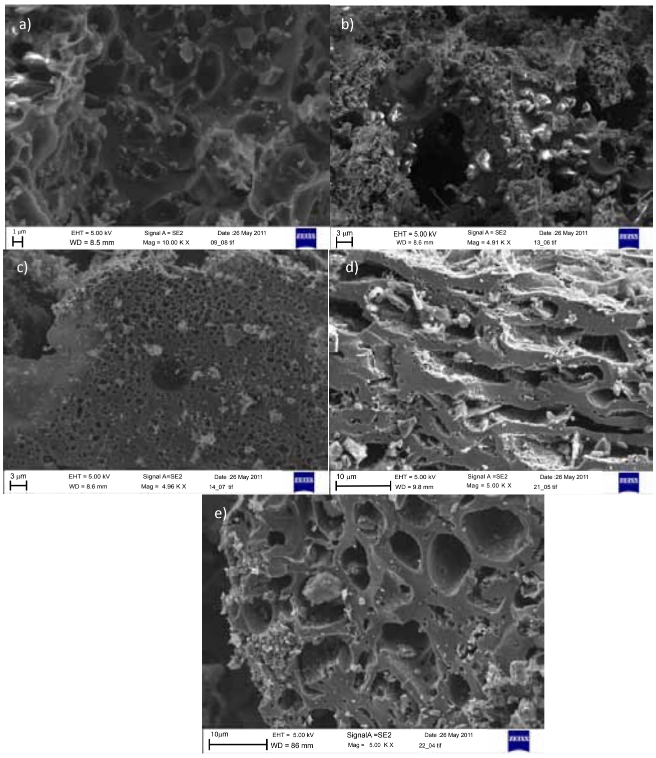

Figure 2: Fe-SEM micrographs a) sample CPH – 09 (0.5-1 mm/KOH/800°C), b) sample CPH – 13 (0.25-0.5 mm/K_2CO_3/800°C), c) sample CPH –14 (0.5-1 mm/K_2CO_3/800°C), d) sample CPH – 21CPH-21 (0.5-1 mm/$ZnCl_2$/500°C), e) sample CPH – 22 (0.25-0.5 mm/$ZnCl_2$/650°C).

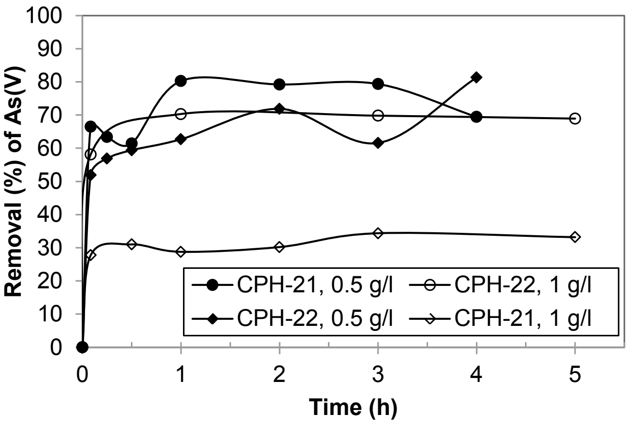

Figure 3: As removal (%) with activated carbons CPH–21 and CPH–22.

Different kinetic models were applied to the experimental data obtained from batch experiments in order to estimate the adsorption mechanism. It was found out that the results followed the best the pseudo-second-order model, which assumes that the rate-limiting step is a chemical sorption between the adsorbate and adsorbent. The integrated form of that model can be written as follows [34]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2)$$

where t is the adsorption time (h), q_t is the amount adsorbed at time t (mg of As / g of AC), k_2 is the pseudo-second-order rate constant (gmg^{-1}h^{-1}) and q_e is the calculated equilibrium adsorption capacity (mg of As / g of AC). The amount of arsenic adsorbed at time t was calculated by using the following mass balance equation:

$$q_t = \frac{(c_0 - c_t)V}{m_{AC}} \qquad (3)$$

where c_0 and c_t are the initial concentration and the concentration at time t of arsenic in solution (mg/l), respectively. V is the total volume of solution (l) and m_{AC} is the mass of activated carbon (g). In Figure 4, (t/q_t) was plotted as a function of time giving linear correlations with all the experimental results.

The second-order adsorption rate constant (k_2) and q_e values were obtained from the slopes and the intercepts. The values of the correlation coefficients, R^2, k_2 and q_e are presented in Table 4.

Conclusions

This research studied the utilization of waste biomass, cocoa pod husk, as a precursor for activated carbon production. The raw material was chemically activated with three different activation agents and characterized for the physico-chemical properties. Five best samples were further studied for the adsorption of arsenic. It was found out that cocoa pod husk is a material that can be used to prepare activated carbon by chemical activation and to obtain adsorption materials with high surface areas.

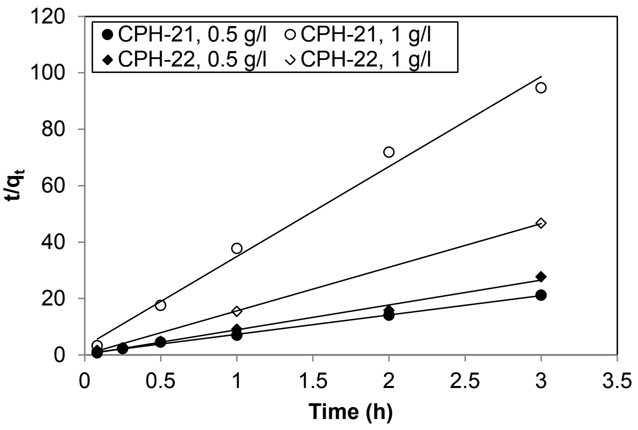

Figure 4: Pseudo-second-order kinetic fitting for the adsorption of As(V) with activated carbons CPH–21 and CPH–22.

Element	Unit	Sample Code				
		CPH – 09	**CPH – 13**	**CPH – 14**	**CPH – 21**	**CPH – 22**
As	(mg/kg)	< 25	< 25	< 25	< 25	< 25
Cd	(mg/kg)	< 25	< 25	< 25	< 25	< 25
Cr	(mg/kg)	< 25	< 25	< 25	< 25	< 25
Cu	(mg/kg)	< 25	< 25	< 25	32	31
Mo	(mg/kg)	< 25	< 25	< 25	< 25	< 25
Pb	(mg/kg)	< 25	< 25	< 25	< 25	< 25
Ca	(g/kg)	12	10	9	0.8	0.7
Zn	(g/kg)	0.3	0.2	0.6	150	93
Fe	(g/kg)	0.4	0.4	0.4	0.06	0.1
Mg	(g/kg)	12	10	10	3	3
K	(g/kg)	110	100	80	1.7	1.8
P	(g/kg)	1.9	2.8	2.3	1.9	2.4
S	(g/kg)	1.3	0.6	1.1	2.1	2.6
Si(*)	(g/kg)	3	1	2	3	3

(*)semiquantitative results

Table 3: Impurities content in the best activated carbons prepared.

AC	Loading (g/l)	k^2 g/(mg·h)	q_e (mg/g)	R^2
CPH-21	0.5	104.3	0.146	0.998
	1	337.6	0.031	0.990
CPH-22	0.5	931.4	0.114	0.990
	1	1709.1	0.065	0.999

Table 4: Pseudo-second-order kinetic constants for As(V) adsorption with two ACs.

$ZnCl_2$ showed to be the best chemical activation agent in the preparation of activated carbon from cocoa pod husk according to the highest BET surface area (780 m^2/g in the best case) and pore volume (0.58 m^3/g in the best case), lowest ash content (6.14 % in the best case), and highest carbon content (86.1 % in the best case), compared with other chemicals.

Activated carbons activated by $ZnCl_2$ are capable to adsorb As(V), up to removal levels of 80 % in less than one hour at the experimental conditions applied (initial pH 6-7, activated carbon concentration 0.5 g/l and 1.0 g/l, initial As concentration 100 ppb).

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References

1. Theivarasu C, Mylsamy S (2010) Equilibrium and Kinetic adsorption studies of Rhodamine-B from aqueous solutions using cocoa (*Theobroma cacao*) shell as a new adsorbent. IJEST 2: 6284-6292
2. Bello O, Ahmad M, Siang T (2011) Utilization of Cocoa Pod Husk for the removal of Remazol Black B reactive dye from aqueous solutions: kinetic, equilibrium and thermodynamic studies. Trends in Appl Sci Research 6: 794-812.
3. Ahmada F, Daudb W, Ahmadc M, Radzi R (2011) Using cocoa (*Theobroma cacao*) shell-based activated carbon to remove 4-nitrophenol from aqueous solution: Kinetics and equilibrium studies. Chem Eng Journal 178: 461– 467.
4. Ahmadpour A (1997) The preparation of activated carbon from macadamia nutshell by chemical activation. Carbon 35: 1723-1732.
5. Adekola F, Adegoke H (2005) Adsorption of blue-dye on activated carbons produced from rice husk, coconut shell and coconut coirpith. Ife J Sci 7: 151-157.
6. Jameel A, Hussain A (2009) Removal of heavy metals from wastewater using activated rice husk carbon as adsorbent. Indian J Environ Protect 29: 263-265.
7. Khan N, Faizal M, Abustan I, Azmier M (2010) Effect of preparation conditions of activated carbon prepared from rice husk by $ZnCl_2$ activation for removal of Cu (II) from aqueous solution. Int J Eng Tech 10: 27-31.
8. Ramakrishnan K, Namasivayam C (2009) Development and characteristics of activated carbons from jatropha husk, an agro industrial solid waste, by chemical activation methods. J Environ Eng Manag 19: 173-178.
9. Malarvizhi R, Sulochana N (2008) Sorption isotherm and kinetic studies of methylene blue uptake onto activated carbon prepared from wood apple shell. J Environ Protect Sci 2: 40-46.
10. Bal’burova TA, Shiretorova VG, Zoltoev EV, Khanturgaeva GI (2008) Production of activated carbons from Pine Nutshells. Russ J Appl Chem 81: 162-164.
11. Aik C L, Qipeng J (2007) Adsorption of phenol by oil-palm-shell activated carbons. Adsorption 13: 129-137.
12. Gueu S, Yao, Adouby, Ado G (2006) Heavy metals removal in aqueous solution by activated carbon prepared from coconut shell and seed shell of the palm tree. J Appl Sci 6: 2789-2793.

13. Kadirvelu K, Kavipriya M, Karthika C, Vennilamani N, Pattabhi S (2004) Mercury (II) adsorption by activated carbon made from sago waste. Carbon 42: 745-752.
14. Rahman IA, Saad B (2003) Utilisation of Guava seeds as a source of activated carbon for removal of Methylene blue from aqueous solution. Malays J Chem 5: 8-14.
15. Hayashi J, Horikawaa T, Takedaa I, Muroyamaa K, NasirAni F (2002) Preparing activated carbon from various nutshells by chemical activation with K_2CO_3. Carbon 40: 2381-2386
16. Moreno C, Carrasco F, Lopez MV, Alvarez MA (2001) Chemical and physical activation of olive-mill waste water to produce activated carbons. Carbon 39: 1415-1420.
17. Bhatnagara A, Sillanpää M (2010) Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment — A review. Chem Eng J 157: 277-296.
18. Azizah A, Nikruslawati N, Swee Tee T (1999) Extraction and characterization of antioxidant from cocoa by-products. Food Chem 64: 199-202.
19. Redgwell R, Trovato V, Merinat S, Curti D, Hediger S, et al. (2003) Dietary fibre in cocoa shell: characterisation of component polysaccharides. Food Chem 81: 103-112.
20. Aregheore E (2002) Chemical evaluation and digestibility of Cocoa (Theobroma cacao) byproducts fed to goats. Trop Anim Health Pro 34: 339-348.
21. Oladayo A (2010) Proximate composition of some agricultural wastes in Nigeria and their potential use in activated carbon production. J Appl Sci Environ Manag 14: 55-58.
22. Tangjuank S, Insuk N, Tontrakoon J, Udeye V (2009) Adsorption of Lead (II) and Cadmium (II) ions from aqueous solutions by adsorption on activated carbon prepared from cashew nut shells. World Acad Sci Eng Technol 52: 110-116.
23. Shukla SR, Sakhardande VD (1992) Column studies on metal ion removal by dyed cellulosic materials. J Appl Polymer Sci 44: 903-910.
24. Orhan Y, Buyukgungor H (1993) The removal of heavy metals by using agricultural wastes. Water Sci Technol 28: 247-255.
25. Kumar U, Bandyopadhyay M (2006) Sorption of cadmium from aqueous solution using retreated rice husk. Biores Technol 97: 104-109.
26. Cem PS, Piew KL, Fun CS (2010) Removal of heavy metals from aqueous solutions by agricultural wastes. World Appl Sci J 9: 412-426.
27. Yoshida T, Yamauchi H, Sun GF (2004) Chronic health effects in people exposed to arsenic via the drinking water: dose–response relationships in review. Toxicol Appl Pharm 198: 243-252
28. Peruvian Ministry of Environment (2008) Supreme Decree No 002-2008-MINAG. Daily *“El Peruano”*. 377222-377227.
29. Lozano D, Lillo MA, Cazorla D, Linares A (2001) Preparation of activated carbons from Spanish anthracite II - activation by NaOH. Carbon 39: 751-759.
30. Lozano D, Lillo MA, Cazorla D, Linares A (2001) Preparation of activated carbons from Spanish anthracite I. Activation by KOH. Carbon 39: 741-749.
31. Ioannidou O, Zabaniotou A (2007) Agricultural residues as precursors for activated carbon production — A review. Renew Sustain Energ Rev 11: 1966-2005.
32. Grossl P, Eick M, Sparks D, Goldberg S, Ainsworth C (1997) Arsenate and chromate retention mechanisms on goethite 2. Kinetic Evaluation Using a Pressure-Jump Relaxation Technique Environ Sci Technol 31: 321-326.
33. Olayinka Kehinde O, Adetunde Oluwatoyin T, Oyeyiola Aderonke O (2009) Comparative analysis of the efficiencies of two low cost adsorbents in the removal of Cr(VI) and Ni(II) from aqueous solution. Afr J Environ Sci Technol 3: 360-369.
34. Ho YS, McKay G (1999) Pseudo-second order model for sorption processes. Process Biochem 34: 451-465.