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# Optimization of Activated Carbon Production from Chicken Manure by Chemical Activation With KOH and $H_3PO_4$

Martha Ruiz-Ojeda, Libia Fonseca, Eliseo Amado-González*

University of Pamplona. IBEAR FJ-207. Research group on alternative and renewable energies.
eamado@unipamplona.edu.co*

The optimization of the parameters for the production of activated carbon from chicken manure was performed by chemical activation with two dehydrating agents: KOH and H3PO4 1:1, 2:1 and 3:1, carbonization temperatures of (350, 400 and 450) °C and residence times of (15, 30 and 45) min. The adsorptive capacity and surface area tests of the active carbon obtained were found. From a surface factorial design response the optimal conditions of the reagent, temperature and residence time were calculated. The amount of dehydrating agent KOH and the combination of dehydrating agent and carbonized temperature showed a significant effect on the preparation process. In the case of H3PO4, only the temperature showed a significant effect with 95% confidence level. The optimal conditions found were: 14 mL of 30 % (w/w) H3PO4 at 450°C for 15 min and 11.6 mL of 30 % (w/w) KOH at 450°C for 30 min.

## 1. Introduction

The agro-industries waste concern environmental risk factors on human health, water supplies air quality (Aunan et al.,1998). Currently different strategies for managing Agro-industries waste by volume reduction were developed (Spahis et al., 2008). A strategy for the conversion of poultry waste was applied in the preparation and characterization of activated carbon (AC) by thermo - chemical and physical activation with carbon dioxide at 800 °C for 30 min (Koutcheiko et al., 2007). The pyrolysis of poultry waste to evaluate the kinetics of degradation was analysed (Kim S., Agblevor, F., 2007). Nowadays, the AC is considered as a better adsorbent for $CO_2$, due to its hydrophobicity properties (Rashidi and Yusup, 2016).
The high surface area of AC makes it appropriate for adsorbing chemical substances form wasted water or air, depending on its structure (Silgado et al., 2014). Chemical activation, a method of producing AC, is a process done in two steps simultaneously: a dehydrating and oxidizing of organic compounds from biomass; and a carbonization and activation at low temperatures (Ioannidou and Zabaniotou, 2007), where the pore development is produced. The dehydrating agent prior to carbonization/activation process most used are: KOH (Guo and Lua, 2007), NaOH (Lillo-Rodenas, 2007), $H_2SO_4$ (Gerçel and Gercel, 2007), $H_3PO_4$ (Nakagawa et al., 2007), $K_2CO_3$ (Carvalho, 2004) and $ZnCl_2$ (Yalcin and Sevinc, 2000), the latter restricted since 1970 for environmental reasons. In the production of AC by chemical activation, the most important variables in the process are: ratio of mixture, carbonization temperature and time (Gratuito et al., 2008). A longer time of activation involves extending the pore size at the expense of surface area; while a smaller activation time reduces energy consumption (Guo and Lua, 2007). In the case of $H_3PO_4$, lower residence time than 30 min, produced an inhibition of the oxidation of coal. However, longer residence time (30-60 minutes), the chemical species bound to the phosphate leaving carbonaceous surface, resulting in degradation of coal (Haimour and Emeish, 2006). The activation temperatures for different biomass was usually between 400-800ºC (Diao et al., 2002); while for other materials it was about 900 °C (Karacan et al., 2007). The optimal activation temperature for coconut shells impregnated with phosphoric acid was 450 ° C (Lainer et al., 2007).
In this work the parameters for the production of Activated Carbons from Chicken manure by Chemical Activation with KOH and $H_3PO_4$ were obtained.

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## 2. Materials and methods

### 2.1 Optimizing the preparation of activated carbon

All reagents were AR-grade chemicals. The chicken manure was dried at 60 °C to remove the moisture and other volatile impurities. Then weighted samples were mixtured with phosphoric acid ($H_3PO_4$) 30 % (w/w) and potassium hydroxide (KOH) 30 % (w/w) for 2 hours at 50 ± 5 ºC. The mixture ratio 1: 5 mL of agent, 2:10 mL of agent, and 3:15 mL of agent were used. Data was fitted to a fractional factorial experimental design to get optimal conditions (Myers and Montogomery, 2002). The variables considered in the process were: mixture ratio, carbonization temperature and residence time of the biomass with dehydrating agent. The levels of these factors were encoded as -1 for the lowest level and 0 to 1 for the intermediate and higher. Table 1 shows the experimental conditions used for each dehydrating agent. A total of 15 experiments were done. Experiments 13 to 15 correspond to the center point replicates design, used to determine the experimental error.

*Table 1: Experimental conditions coded from 1 to 15. A fractional factorial experimental design was used for optimization.*

| *Experiments* | *Coded level* | | | *Mixture ratio* | *Residence time(t) min* | *Temperature (T) ºC* |
|---|---|---|---|---|---|---|
| | *R. I.* | *t* | *T* | | | |
| *1* | *-1* | *-1* | *0* | *1* | *15* | *400* |
| *2* | *-1* | *1* | *0* | *1* | *30* | *400* |
| *3* | *1* | *-1* | *0* | *3* | *15* | *400* |
| *4* | *1* | *1* | *0* | *3* | *45* | *400* |
| *5* | *-1* | *0* | *-1* | *1* | *30* | *350* |
| *6* | *-1* | *0* | *1* | *1* | *30* | *450* |
| *7* | *1* | *0* | *-1* | *3* | *30* | *350* |
| *8* | *1* | *0* | *1* | *3* | *30* | *450* |
| *9* | *0* | *-1* | *-1* | *1* | *15* | *350* |
| *10* | *0* | *-1* | *1* | *1* | *15* | *450* |
| *11* | *0* | *1* | *-1* | *2* | *45* | *350* |
| *12* | *0* | *1* | *1* | *2* | *45* | *450* |
| *13* | *0* | *0* | *0* | *2* | *30* | *400* |
| *14* | *0* | *0* | *0* | *2* | *30* | *400* |
| *15* | *0* | *0* | *0* | *2* | *30* | *400* |

R.I.: ratio of the mixture. 1: 5 mL of agent. 2:10 mL of agent. 3:15 mL of agent.
T: temperature.
t: residence time.

### 2.2 Characterization of activated Carbon.

**Adsorptive capacity:** Determined by ASTM D3860-98, 2014 (isotherm technique in aqueous phase). Methylene blue was used as adsorbate (ASTM, 2014).

**Surface area:** It was calculated from the iodine value, according to ASTM standard D4607- 94, 2006. The iodine value defined as the number of mg of iodine adsorbed from an aqueous solution per 1 g of AC when the iodine concentration in the filtering is 0.002N (ASTM, 2006).

## 3. Results and discussion

### 3.1 Optimization of the conditions of preparation of activated carbon.

Table 2 shows a higher activity for AC prepared with $H_3PO_4$ in experiment No. 8 with next conditions: ratio of thje mixture 3: dehydrating agent added 15 mL; residence time of 30 min at 450 °C. An activity of 3772.2 for the AC was obtained using 30 % (w/w) $H_3PO_4$. In the case of AC obtained with KOH, it was found that for the

experiment No. 6 with the next conditions: ratio of mixture 1: 5 mL dehydrating agent, residence time of 30 min at 450°C. A maximum value of activity was obtained of 3789.1.
Table 3 displays the analysis of variance, ANOVA. The variables were: added amount of dehydrating agent, carbonization temperature and residence time. The relationship between ratio of mixture and ratio of mixture-temperature relationship interaction in the process of preparing AC with 30 % (w/w) $H_3PO_4$ was considered for a significance level $p<0.05$. In the preparation of AC with 30% (w/w) KOH the parameter temperature showed an effect with a significant level of 95%.

*Table 2. Activities based on the ratio of mixture conditions, temperature and time of carbonization*

| *Experiments* | *Activity* | |
|---|---|---|
| *No.* | 30 % (w/w) $H_3PO_4$ | 30% (w/w) KOH |
| *1* | *3596.5* | *3282.8* |
| *2* | *3110.2* | *3492.9* |
| *3* | *3730.8* | *3541.1* |
| *4* | *3303.4* | *3668.4* |
| *5* | *3730.6* | *3606.7* |
| *6* | *2911.3* | *3789.1* |
| *7* | *3210.4* | *3448.1* |
| *8* | *3772.2* | *3723.4* |
| *9* | *3634.1* | *3420.5* |
| *10* | *3730.8* | *3654.8* |
| *11* | *3709.7* | *3623.6* |
| *12* | *3640.8* | *3744.6* |
| *13* | *3664.9* | *3716.5* |
| *14* | *3651.2* | *3620.2* |
| *15* | *3713.3* | *3672.2* |

*Tabla 3: Analysis of variance for activity*.

| *Variable* | *Relationship F* | | *Value p* | |
|---|---|---|---|---|
| | *Acid* | *Base* | *Acid* | *Base* |
| *A: Added amount of agent* | *2.46* | *0.45* | *0.1774* | *0.5300* |
| *B: Temperature* | *0.29* | *6.84* | *0.6130* | *0.0473* |
| *C: Time* | *4.75* | *4.11* | *0.0812* | *0.0983* |
| *AA* | *10.75* | *1.55* | *0.0220* | *0.2681* |
| *AB* | *21.02* | *0.18* | *0.0059* | *0.6901* |
| *AC* | *0.04* | *0.14* | *0.8527* | *0.7215* |
| *BB* | *0.03* | *0.58* | *0.8713* | *0.4820* |
| *BC* | *0.30* | *0.27* | *0.6063* | *0.6282* |
| *CC* | *0.04* | *3.19* | *0.8487* | *0.1340* |

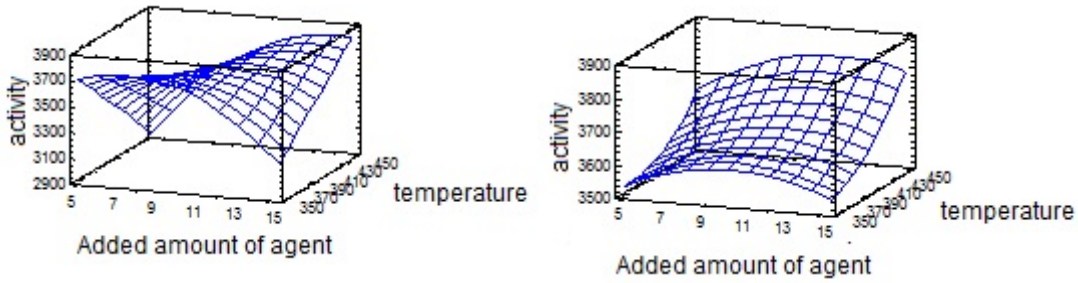
In the figure 1 the response surface obtained from optimization of the preparation of AC with a) 30 % (w/w) $H_3PO_4$ and b) 30 % (w/w) KOH. Table 4 shows the best experimental parameters conditions for the process of preparing AC.
Eq (1) is obtained from the response surface fitted, the activity of AC with 30 % (w/w) $H_3PO_4$:

$$A(H_3PO_4) = 7071.99 - 336.004*C - 8.45414*T + 8.17489*t - 10.2799*C^2 + 1.38105*CT + 0.196362*Ct - 0.00534387*T^2 - 0.0551774*Tt + 0.0699664*t^2 \quad (1)$$

Eq (2) is obtained from the surface response fitted for the preparation of activated carbon with 30 % (w/w) KOH:

$$A(KOH) = 4566.77 + 33.3464*C - 11.6533*T + 50.3572*t - 2.84835*C^2 + 0.0928662*CT - 0.276222*Ct + 0.017362*T^2 - 0.0377512*Tt - 0.454034*t^2 \quad (2)$$

Where
A = activity
C = added amount of dehydrating agent
T = temperature
t = time




a) b)

*Figure 1. Surface response optimization for production of AC with a*) 30% (w/w) $H_3PO_4$ and b) 30% (w/w) KOH.

*Table 4: Optimum operating conditions for the AC production form chicken manure.*

| *Factors* | *Level* | | *Optimum Value* | |
|---|---|---|---|---|
| | *Lower* | *higher* | *acid* | *Base* |
| *Adder amount of agent, mL* | *5* | *15* | *14* | *11,6* |
| *Temperature, ºC* | *350* | *450* | *450* | *450* |
| *Time, min* | *15* | *45* | *15* | *33* |

**3.2 Characterization of AC**

Adsorptive capacity. Table 5 display the results for the isotherms of AC prepared with $H_3PO_4$ 30% (w/w) and KOH 30% (w/w) using concentrations of methylene blue. A standard procedure was used (Brahima et al., 2014). Batch adsorption experiments were done with 50 mL glass bottles containing a weight mass of AC and 8 mL of dye solution. The initial concentration of dye was varied from 10 to 100 mg.L-1. The glass bottles were agitated in orbital shaker by three hours and centrifugated at 7000 rpm for 30 min. The optical measurements were done with a spectrophometer DU-70 Beckman at 663 nm.

Surface area. This parameter indicates the absorption capacity of the carbon for the iodine and is dependent on both the concentration of iodine in the solution, and the amount of activated carbon. Table 6 shows the data obtained from the isotherms iodine number of activated carbon prepared with $H_3PO_4$ and KOH, using concentrations of iodine solutions.

*Table 5: Data obtained from activated carbon isotherms.*

| *AC isotherms with methylene blue* | | | |
|---|---|---|---|
| 30 % (w/w) $H_3PO_4$ | | 30 %(w/w) KOH | |
| *Activity (mg/g)* | *Concentration (ppm)* | *Activity (mg/g)* | *Concentration (ppm)* |
| 8,367 | 2,31 | 8,07 | 2,82 |
| 12,30 | 4,81 | 12,05 | 8,28 |
| 15,38 | 6,78 | 12,99 | 9,58 |
| 20,71 | 10,11 | 16,83 | 14,84 |

*Table 6: Data obtained from the isotherm iodine number of AC.*

| *Activated Carbon isotherms, in iodine index* | | | |
|---|---|---|---|
| 30% (w/w) $H_3PO_4$ | | 30% (w/w) KOH | |
| *Activity (mg/g)* | *Concentración (ppm)* | *Activity (mg/g)* | *Concentration (ppm)* |
| 841.2 | 1.129x10-2 | 832.8 | 1.030x10-2 |
| 956.4 | 2.038x10-2 | 968.0 | 2.127x10-2 |
| 1082 | 3.030x10-2 | 1093 | 3.141x10-2 |

## 4. Conclusions

The parameters for process of AC production were optimized from chicken manure by a factorial design surface fractional response, using dehydrating agent 30% (w/w) $H_3PO_4$ and 30% (w/w) KOH. The parameters studied were the added amount of the reagent, temperature and residence time. The production of AC with 30% (w/w) $H_3PO_4$ showed that the quantity of dehydrating agent and the dehydrating agent-temperature combination were significant on the preparation process, $p < 0.05$. In the case of production of AC with 30% (w/w) KOH, only the temperature, $p < 0.05$.

The best conditions of the parameters for the process were: 14 mL of 30% (w/w) $H_3PO_4$, 450 °C for 15 min, and 11.6 mL of 30% (w/w) KOH at 450 °C for 30 min.

AC prepared with 30% (w/w) $H_3PO_4$ had a higher adsorptive capacity than AC prepared with 30% (w/w) KOH, but the analysis of surface area showed that the AC made with 30% (w/w) KOH had larger area.

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