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Catalytic oxidation of aqueous methyl and dimethylamines by activated carbon

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The catalytic wet air oxidation (CWAO) of methyl and dimethylamines was studied. A commercial peach stones activated carbon and its oxidized and reduced forms were used as catalysts. The observed catalytic behavior is related to the presence of oxygenated surface functional groups on the activated carbons. The N-compounds were selectively oxidized to nitrogen, water and carbon dioxide using these activated carbon catalysts. It is proposed that the quinonic surface groups are responsible for the selective catalytic oxidation of these amines. Carboxylic, lactonic and anhydride groups strongly adsorb the amine compounds producing inhibition of the catalytic activity of the activated carbon in the CWAO process.

KEY WORDS: activated carbon; CWAO; methylamine; dimethylamine; wet oxidation

1. Introduction

The problems that many chemical causes on environment such as ground water, air and human health are well known. In the case of nitrogen compounds like aqueous ammonia, water eutrophication has been studied using different methods [1,2]. The catalytic technology is an alternative that involves the transformation of the nitrogen-compounds to molecular nitrogen like in catalytic wet air oxidation (CWAO) [3–5]. The active phases used in the catalysts are mainly noble metals, Ru, Rh, Pt, Pd, Ag supported on Al_2O_3, SiO_2, TiO_2 among others [3–8]. Activated carbons have been used as catalysts in the ammonia CWAO process with good result [5,8]. Aliphatic amines such as methylamine and dimethylamine, are toxic compounds in very small concentrations [9]. They are produced as contaminants in different industrial processes such as fish meal plants and nitrogen dyes degradation [10–11]. Information related to the treatment of aliphatic primary amines into biodegradable or friendly compounds is very scarce. In some processes the degradation of aliphatic amines is only up to ammonia [12], cyanides or others [13,14], but not to molecular nitrogen. Activated carbons have been widely used in different processes in order to improve environmental conditions, mainly due to their different textural and chemical properties. They can be manufactured with high surface areas, tailored pore distribution, and different oxygenated surface groups thus producing materials with remarkable catalytic and adsorption properties.

In previous works we have used peach stones activated carbons in solution adsorption of metal ions and organo-chlorinated compounds [15–17]. Recently we have reported the use of peach stones activated carbons in adsorption and CWAO process of aqueous ammonia [8]. From these studies the influence of the surface functional groups present in these materials together with textural properties have been established. In this work the application of peach stones activated carbons in the CWAO process of methylamine and dimethylamine was studied. The catalytic behavior is related to the different surface functional groups present on the activated carbons.

2. Experimental

2.1. Activated carbons

A commercial activated carbon (CUDU 1000) manufactured by Petrochil S.A. (Chile) from peach stones was used. The modification of the original activated carbon by oxidation was carried out in 6 M HNO_3 at 80 °C using 1 g carbon/10 mL solution during 1 h. The treated carbon was thoroughly washed until complete elimination of residual HNO_3. The reduction was carried out at 400 °C for 10.5 h with a hydrogen flow of 50-mL/min [8]. Table 1 shows the nomenclature of the activated carbons used.

2.2. Chemical analysis

Acid-base titration using a mixture of methyl red and bromocresol green as indicator [18] determined the methyl and dimethylamine concentrations. The analysis was previously validated by molecular absorption spectrometry using the Merk Spectroquant method, 1.14752.001 [19]. The CWAO reaction products, oxygen, nitrogen, and carbon dioxide in the gas phase were chromatographycally determined using a molecular sieve 13× column for O_2 and N_2, and a Porapak Q column for CO_2. Total oxidation products like nitrate and nitrite were analyzed by colorimetric methods [20].

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Table 1
Modification conditions and nomenclature of activated carbons

Activated carbon	Modification process Oxidation	 Hydrogenation	 Name
CUDU 1000	No	No	C
Oxidized activated carbon	Yes	No	COX
Hydrogenated activated carbon	No	Yes	CH
First hydrogenated and later oxidized activated carbon	Yes	Yes	CHO
First oxidized and later hydrogenated activated carbon	Yes	Yes	COH

2.3. *Catalysts characterization*

The textural characterization of activated carbons was obtained by nitrogen adsorption at 77 K using Micromeritics Gemini 2370 equipment. From these data, the following characterization parameters were calculated. Apparent surface areas from Brunauer, Emmet and Teller model (S_{BET}); micropore volume using Dubinin–Radushkevich equation (Vo); pore volume from nitrogen adsorbed at 0.95 of relative pressure (V_P) and mesopore volume (Vm) calculated as the difference between pore volume and micropore volume [21].

The chemical characterization of activated carbons surface groups was obtained by thermal programmed decomposition (TPD), Boehm method, Fourier transform infrared spectroscopy (FTIR), zero point charge (ZPC) and pH slurry as described in [8].

2.4. *Adsorption of methyl and dimethylamine on activated carbons.*

Equilibrium adsorption studies were carried out varying the amine concentration from 50 to 3000 ppm at 30 °C. A mass of 0.2 g of dry activated carbon was contacted with 50 mL of amine solution in an isothermal shaker. After 24 h of contact, the solution was separated from the activated carbon, and the residual concentration of amines was analyzed.

2.5. *Catalytic activity essays*

Reactions were carried out in a pressurized Parr reactor of 300-mL capacity. A volume of 150 mL of amine at 1000 ppm of concentration was contacted with activated carbons according to the experimental conditions shown in Table 2. The adsorption of methyl and dimethyl amines under CWAO were done in the same conditions as the activity essays shown in Table 2 except that they were performed under N_2 atmosphere. In order to minimize external and internal mass transfer effects under CWAO conditions, several experiments were carried out. Experiments at various particle size (0.6–2) mm, agitation speeds (250–750 rpm), and activated carbon mass to solution volume ratios (0.75–1.5) were performed.

Table 2
Reaction conditions of methylamine and dimethylamine decomposition by CWAO process

Temperature	195 °C
Pressure	16 atm.
Time	0.25–2 h
Methylamine$_{(aq)}$ and dimethylamine$_{(aq)}$ concentration	1000 mg/L
Ratio[a]	1/150
Atmosphere[b]	O_2 or N_2
Size particle (mm)	1–2

[a] Ratio: Activated carbon mass (g)/Solution volume (mL).
[b] CWAO Activity assays were performed under O_2 atmosphere, and adsorption assays under N_2 atmosphere.

3. Results and discussion

3.1. *Adsorption isotherms of amines on activated carbons*

Figure 1 shows the equilibrium adsorption isotherms of methyl and dimethyl amine on different activated carbons, in aqueous solutions, at 30 °C. As can be seen in Table 3, all the activated carbons have similar textures. Therefore the surface chemical properties are the main factor that explains the differences observed in the amines adsorption on these activated carbons. Figure 2 contains TPD profiles of most representative activated carbons, showing the differences in their surface functional groups. Table 4 summarizes the results obtained from TPD, FTIR, Boehm and ZPC methods, which characterized the chemical surface properties of the activated carbons.

From figure 1 it is observed that both organic compounds are better adsorbed on the activated carbons previously oxidized. These results are in agreement with the largest amounts of superficial functional groups that decompose at low temperatures present in the carbons COX and CHO. Thus the adsorption of the amines occurs mainly due to their interactions with carboxylic, lactonic, and anhydride like surface groups. Nevertheless when the low temperature groups are present in small amounts, the high temperature groups have a role in the adsorption of the amine compounds. As can be seeing in figure 1, the activated carbon named COH that presents higher amounts of high temperature functional groups, shows higher amine adsorption than the original carbon. A similar behavior was found in the case of aqueous

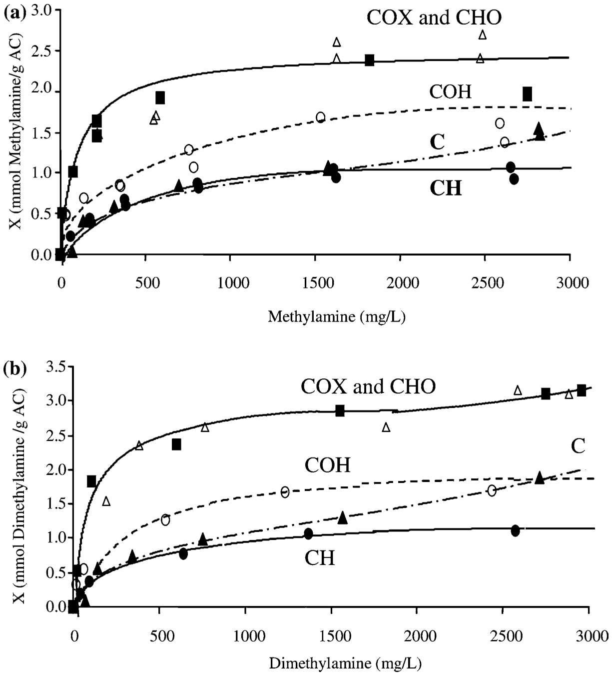

Figure 1. Adsorption isotherm at 30 °C and atmospheric pressure: (1a) Methylamine and (1b) Dimethylamine (▲C, ■ COX, ● CH, ○ COH, ♠CHO).

Table 3
Textural characterization of activated carbons

Activated carbon	S_{BET} m^2/g	Vo cc/g	Vm cc/g
C	969	0.42	0.05
COX	958	0.41	0.05
CH	914	0.41	0.05
CHO	975	0.44	0.04
COH	979	0.44	0.05

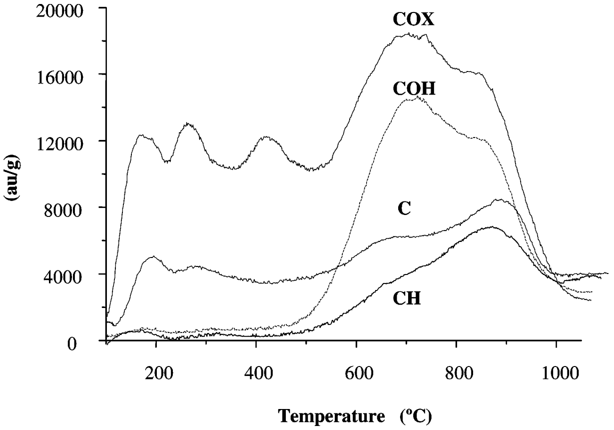

Figure 2. Thermal programmed decomposition (TPD) of representative activated carbons.

ammonia adsorption, where the oxidized carbons adsorb larger amounts of the solute than the untreated or reduced carbon [8]. However, the amine compounds adsorption is larger than ammonia adsorption. Hydrogen substitution by methyl groups in ammonia produces an inductive effect that generates a polarization between the methyl(s) and amino groups, and increases the basic character of the N-compounds in the following order: dimethylamine > methylamine > ammonia with pK_b values of 3.28, 3.36, and 4.74, respectively [22–24]. Moreover the most basic N-compounds have a higher interaction with high temperature surface groups, like carbonyls, increasing the adsorption due to the carboxylic like groups. So the adsorption of methyl and dimethyl amine would occur not only by the interaction with low temperature decomposing groups but also by interaction with carbonyl groups, that decompose at higher temperatures.

Carbonyl groups concentration on activated carbons followed the order COX ≅ CHO > COH > C > CH a tendency that is similar to the adsorption trend shown by the amino compounds onto these activated carbons. The adsorption isotherms profiles can be considered type L according to Giles *et al.*, [25] classification this means that there is not a strong competition between the solvent and the N-compounds for the activated carbon adsorption sites.

3.2. Oxidation of methyl and dimethyl amines by the CWAO process

The results of the experiments carried out to minimize external and internal mass transfer effects under CWAO conditions showed that diffusional effects were not important when using particle size of 1–2 mm, a ratio of 1 g C/150 mL solution, 500 rpm of agitation speed.

The catalytic activity of activated carbons in the CWAO process of methyl and dimethyl amine can take place by selective or total oxidation of the N-compounds. The selective oxidation of the amino group to molecular nitrogen and the total oxidation of methyl groups to carbon dioxide, can be described by the following global reactions:

$$4CH_3NH_2 + 9O_2 \rightarrow 2N_2 + 4CO_2 + 10H_2O \quad (1)$$

$$4(CH_3)_2NH + 15O_2 \rightarrow 2N_2 + 8CO_2 + 14H_2O \quad (2)$$

Under the experimental conditions used there was no production of carbon monoxide in the CWAO of methyl and dimethyl amines with activated carbons C, COX and COH, showing that the methyl groups were completely oxidized to CO_2 and H_2O. It is important to mention that the mass of the activated carbons did not change during the CWAO reactions indicating that activated carbon combustion was not observed or it is negligible. Also, the DTP analysis of activated carbons performed before and after CWAO reactions showed only small modifications of the surface functional groups.

It is observed, as shown in figure 3, that under the same experimental conditions methylamine conversion is higher than that of dimethylamine. The lower CWAO

Table 4
Summary of surface groups on activated carbons

Activated carbon	Lower-temperature decomposition	Higher-temperature decomposition
C	Middle amounts of Carboxylic, anhydride and lactonic	Middle amounts of carbonyl, higher-temperature anhydride, quinonic
COX and CHO	Largest amounts of Carboxylic, anhydride and lactonic	Largest amounts of phenolic, carbonyl, higher-temperature anhydride and quinonic
CH and COH	Very low amounts of Carboxylic, anhydride and lactonic	Larger amounts of phenolic, carbonyl, quinonic and higher-temperature anhydride

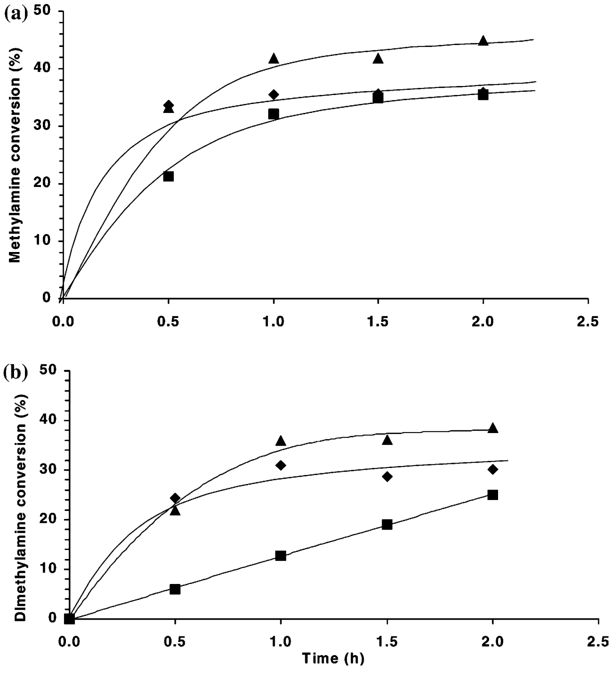

Figure 3. Methyl- (3a) and dimethyl-amine (3b) conversion's in the CWAO process at 195 °C and 1/150 g cat/mL solution (♦ C, ■COX, ▲ COH).

activity observed for dimethylamine can be explained by both its strong adsorptions on the activated carbons due to its higher basicity and some steric hindrance that will diminish oxygen adsorption. The N-compounds' oxidation in the CWAO process may be explained by a first step of N-compounds adsorption together with oxygen adsorption in neighboring sites. In the adsorbed state the carbon of methyl groups, hydrogen and oxygen atoms are activated and they may react forming nitrogen, carbon dioxide and water. The effect of a strong adsorption is enhanced on activated carbon COX that has higher amounts of carboxylic like groups. The reduction of the catalytic activity for dimethylamine in the CWAO processes due to the strong interaction with carboxylic like groups are also observed for methylamine but by a lesser extent.

The results presented in Table 5 show that on these activated carbons a simultaneous strong adsorption of amines, and the CWAO reaction to nitrogen and carbon dioxide occurs. The methyl and dimethyl amines treated under CWAO conditions but in the absence of catalyst did not show any change in their initial concentrations; the uncatalyzed decomposition of these amine compounds did not occurred. The amounts of methyl and dimethyl amines strongly adsorbed by the activated carbons under CWAO conditions was higher for COX. The functional surface groups that decomposed at low temperatures were found to strongly adsorb ammonia in the CWAO process [8]. Since methyl and dimethylamine are chemically similar to NH_3, it is likely that these compounds are also strongly adsorbed by surface functional groups similar to those observed in ammonia adsorption essays previously reported; that is carboxylic, lactonic and anhydride. Thus, the activated carbon that has the largest amounts of low temperature surface groups (COX) adsorbs the largest quantities of aliphatic amines. The important adsorption increment of methyl- and dimethyl-amine by carbons COH and C with time, as shown in Table 5, can be attributed to an increase of functional groups when the carbons were immerse in the aqueous media, in nitrogen atmosphere, under CWAO conditions. TPD profiles of the activated carbons after CWAO treatment, under nitrogen atmosphere, showed changes of the surface functional groups. A higher increase of the high temperature surface groups was observed for the activated carbon C.

Conversion of nitrogen and carbon dioxide under CWAO condition at 195 °C, shown in Table 5, are in agreement with the stoichiometry of equations 1 and 2; carbon dioxide to nitrogen ratio is nearly 2 for methylamine and 4 for dimethylamine.

In the partial oxidation of ammonia by CWAO it was proposed that surface quinonic groups participate in the oxidation process and that ammonia adsorption on the carboxylic like sites have a negative effect upon the catalytic activity [8]. As shown above methyl and dimethyl amine are best adsorbed than ammonia on the carboxylic like sites present on activated carbons; thus the negative effect observed in ammonia conversion has increased in the case of these amines. Also, it is likely that some ammonia could have been formed during the CWAO of amines, but previous result of ammonia

Table 5
Catalytic activity of carbons C, COH and COX in CWAO of methyl-amine and dimethyl-amine at 195 °C

Activated carbon	Reaction time h	Methylamine				Dimethylamine			
		Conversion to N_2 mmol/g	Conversion to CO_2 mmol/g	Adsorption in CWAO conditions mmol/g	Nitrite + Nitrate mmol/g	Conversion to N_2 mmol/g	Conversion to CO_2 mmol/g	Adsorption in CWAO conditions mmol/g	Nitrite + Nitrate mmol/g
COH	0.5	1.48	2.87	0.53	n.d.	0.67	2.56	0.71	n.d.
	1.0	1.85	3.60	0.60	n.d.	1.09	4.25	0.78	n.d.
	1.5	1.86	3.51	0.76	n.d.	1.10	4.26	0.98	n.d.
	2.0	2.00	3.76	0.74	0.003	1.56	5.84	0.84	0.005
COX	0.5	0.94	1.81	1.49	n.d.	0.18	0.70	1.37	n.d.
	1.0	1.42	2.78	1.36	n.d.	0.39	1.51	1.64	n.d.
	1.5	1.62	2.87	1.44	n.d.	0.59	2.24	1.65	n.d.
	2.0	1.54	2.94	1.52	0.005	0.76	2.92	1.69	0.010
C	0.5	1.49	2.91	0.42	n.d.	0.75	2.89	0.81	n.d.
	1.0	1.57	3.00	0.78	n.d.	0.94	3.51	1.00	n.d.
	1.5	1.52	2.90	0.94	n.d.	0.87	3.39	1.20	n.d.
	2.0	1.54	2.94	0.96	0.001	1.22	4.72	0.96	0.007

n.d.: not determinated.

CWAO under the same experimental conditions (195 °C, using the same activated carbons) have shown that ammonia was completely converted to nitrogen and water [8]. Total oxidation products such as nitrite and nitrate, found after two hours of reaction, was in all cases lower than 0.3% of the total conversion. The higher nitrites and nitrates formation occurs when large concentrations of methyl and dimethyl amine are strongly adsorbed. This is best observed for carbon COX in the oxidation of the most basic compound, dimethylamine. These results, under the reaction condition, indicate that when aliphatic amines are strongly adsorbed the total oxidation products may occur by secondary reactions.

4. Conclusions

Methyl and dimethyl amine adsorption under environmental conditions takes place mainly over carboxylic, lactonic and anhydride surface groups of activated carbons. It is also possible that amines adsorption occur on the carbonyl groups especially in the case of dimethylamine because of its higher basic strength.

In the oxidation of amine compounds by the CWAO process, the results obtained suggest the catalytic role of the quinonic surface groups in the transformation of these N-compounds to nitrogen. On the other hand, carboxylic like surface groups strongly adsorb this amine compounds producing inhibition of the catalytic activity. The activated carbons with higher catalytic activity are those that have smaller amount of low temperature surface groups (carboxylic like) and important amount of high temperature groups (quinonic). The peach stones activated carbons, under the experimental conditions used, resulted to be highly selective catalysts for the CWAO process of this amine compounds.

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