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Effect of oxidative modification of activated carbon for the adsorption behavior of nicotine

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ABSTRACT

The adsorption of nicotine onto activated (AC) and AC modified (MAC, by contact with ammonium persulfate) can be described well using the Langmuir model with maximum adsorption capacities of 552 and 640 mg g^{-1}, respectively. Nicotine has high 'hardness' and appears to adsorb most readily on the increased concentration of 'hard' MAC edge functional groups. Adsorption is shown to be exothermic; with enthalpy of −10 and −16 kJ mol^{-1} for AC and MAC, respectively. The negative free energy and positive entropy of adsorption indicate a spontaneous process and a strong affinity between aqueous nicotine and AC or MAC.

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Introduction

China is the world's largest tobacco producing country with output reaching 2.56 million tons annually. This accounts for 30% of the world's production of 8.53 million tons. The processing of tobacco for manufacture of cigarettes results in approximately 33% of the tobacco being wasted. However, in recent years there have been technological developments enabling utilisation of this tobacco waste to produce tobacco slice. As for the process of papermaking, large amounts of water are required to produce tobacco slice. For example, 70 t of wastewater will be created for production of 1 t of tobacco slice [1]. The wastewater contains considerable amounts of organics including proteins, carbohydrates, cellulose, organic acid, tobacco tar and nicotine [2] and is considered to be very difficult to remediate. In particular, nicotine in wastewater, which is the main alkaloid in tobacco, is toxic for most microorganisms. Aerobic biodegradation is widely used for treating wastewater but this is not effective for tobacco wastewater due to the presence of nicotine. Much of the research on treatments for tobacco wastewater treatment have focused on screening for nicotine-degrading bacteria although the screening process itself may be high cost and labor intensive. *Pseudomonas* sp. ZUTSKD [3], *Agrobacterium* sp. Strain S33 [4] and *Rhodococcus* sp. Y22 [5] have been identified as possible effective microorganisms but implementation is expensive.

Development of a methodology that can remove nicotine is required to improve the efficiency of aerobic biodegradation as an alternative to treatment by nicotine-degrading bacteria. Adsorption is the most common method used in the treatment of wastewater. For example, zeolites [6], carbon nanotubes [7], bentonite [8] and periodic mesoporous organosilicas [9] have been investigated as possible adsorbents for the treatment of nicotine containing wastewater. However, according to current research, in comparison activated carbon offers either greater adsorption efficiency or lower adsorption cost. Activated carbon as an effective adsorbent, with an high degree of porosity and extensive surface area, is widely used in dye wastewater treatment [10,11] and is known to be able to remove nicotine from tobacco wastewater [6]. The adsorption capacity of activated carbon is attributed to its textural properties and the chemical nature of its surface, i.e. the amount and nature of the oxygen-containing functional groups [12]. In this study, we report the adsorption behavior of nicotine on activated carbon before and after its modification, and interpret how the acidic functional groups affect this behavior.

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Experimental

Materials and chemicals

Activated carbon, nicotine with the purity of 99 wt.% and other chemicals, provided by Hongyun Co. Ltd., Wuhan, China, were of analytical reagent grade. The activated carbon was passed through a 200 mesh sieve before being stored in a dryer.

Modification of activated carbon

For modification, activated carbon (AC) was mixed, at solid-to-liquid ratio (S/L) of 1:6 (mass to volume, g mL^{-1}), with 1 mol L^{-1} ammonium persulfate solution for 4 h at 60 °C. After oxidation, the activated carbon was washed with distilled water until almost all the sulfate was removed. The residual sulfate was determined using barium chloride. The modified activated carbon (MAC) was then dried for 24 h at 120 °C.

Chemical and physical characteristics of adsorbent and adsorbate

Identification and quantification of the various functional groups on the activated carbon was determined using the Boehm method [13]. To do this 0.5 g of either the AC or MAC was added to 25 mL of 0.05 mol L^{-1} alkali solution, composed of NaOH, Na_2CO_3 or $NaHCO_3$, and was shaken reaction for 24 h. The solution was then passed through 0.45 μm filter paper and the filtrate was titrated using 0.1 mol L^{-1} HCl solution.

The pH of the point of zero charge (pH_{pzc}) was obtained using the pH drift method [12]. This was done by adjusting the pH of 50 mL of 0.01 mol L^{-1} NaCl solution by unit values from 2 to 12 by addition of different concentration of H_2SO_4 or NaOH solutions. 0.15 g of AC or MAC was added to these solutions and the final pH was measured (PHS-3C, China) until there was no further changes; typically 24 h at 25 °C. The pH_{PZC} is the point where the curve pH_{final} versus $pH_{initial}$ crosses the line $pH_{initial} = pH_{final}$. The textural properties of specific surface area, total pore volume, microporous pore volume and average pore diameter were measured as per Gregg, Sing and Salzberg [14] and Haghseresht and Lu [15].

Nicotine is a 3-substituted pyridine. Its chemical structure consists of one 6-membered (pyridine) and one 5-membered (pyrrolidine) ring (Fig. 1). As a weak organic base, its alkalinity is mainly attributed to the acceptor sites of the two nitrogen atoms located on the pyridine and pyrrolidine rings. *N*-methyl-pyrrolidine is a stronger electron donor than N-pyridine, resulting in stronger alkalinity. The dissociation constants (p*K*a) of *N*-methyl-pyrrolidine and N-pyridine are 8.02 and 3.12, respectively [6]. Therefore, nicotine can exist in water in three possible forms depending on pH: neutral, mono- and bi-cationic. The bi-cationic form occurs predominantly when the pH is less than 3. At pH from 5 to 8 the mono-cationic form, due to the protonation of *N*-methyl-pyrrolidine, is predominant. When the pH is greater than 10, nicotine exists mainly in the neutral form.

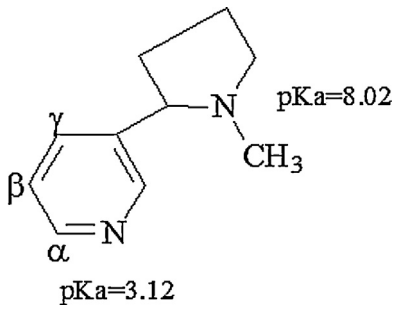

Fig. 1. The chemical structure of nicotine and its dissociation constants.

Nicotine isothermal adsorption experiments

Equilibrium adsorption of nicotine onto AC or MAC was measured at 30, 40 and 50 °C. To do this 0.25 g AC or MAC was added into erlenmeyer flasks containing 50 mL of nicotine solution (in distilled water) varying in concentration from 200 to 5000 mg L^{-1}. The flasks were then placed into a constant temperature vibrator vapour-bath (SHZ-82A, China) and shaken at 200 rpm for 30 min. After equilibration, the solution was passed through 0.45 μm filter paper and the residual nicotine in the filtrate was analysed using UV/visible spectroscopy (SP-752, China) at 259 nm. Each experiment was carried out in duplicate. The equilibrium adsorption capacity, Q_e (mg g^{-1}), of nicotine on AC and MAC was calculated in the following equation:

$$Q_e = \frac{V(C_0 - C_e)}{M} \quad (1)$$

C_0 and C_e represent the initial and equilibrium concentrations of nicotine (mg L^{-1}); V and M are the volume of solution (L) and the mass of AC or MAC (g) added initially, respectively.

Nicotine adsorption experiments at different pH

The effect of solution pH on nicotine adsorption was examined at 30 °C. 0.25 g AC or MAC was added into erlenmeyer flasks containing 50 mL of 1000 mg L nicotine solution at specific pH which were then shaken for 30 min. The initial pH prior to AC or MAC addition was adjusted by the addition of H_2SO_4 or NaOH solutions to be across the range of 2–13. After equilibration the solution was filtered and the residual nicotine concentration was determined by the method described in the Chemical and physical characteristics of adsorbent and adsorbate section [5,6].

Results and discussion

The variation of chemical and physical characteristics between AC and MAC

The chemical characteristics of AC and MAC listed in Table 1 indicate that there are significant differences in the surface concentrations of the acidic functional groups, in particular the concentration of carboxyl and phenol are greater in MAC, as is consistent with Langley and Fairbrother [16]. It is also observed that the pH_{pzc} decreased from 6.3 for AC to 4.8 for MAC, most likely due to this increase in concentration of acidic functional groups. In contrast the oxidation process has little effect on physical characteristics (Table 2) with the porous structure of AC and MAC being nearly the same [17].

Table 1
Acidic functional groups (mmol g^{-1}) and pH_{pzc} of activated carbon.

	Carboxyl	Lactone	Phenol	Total acid	pH_{pzc}
AC	0.14 ± 0.02	0.07 ± 0.01	0.05 ± 0.01	0.26 ± 0.04	6.3 ± 0.05
MAC	0.20 ± 0.03	0.08 ± 0.02	0.15 ± 0.01	0.43 ± 0.06	4.8 ± 0.08

Table 2
Textural properties of activated carbon.

	BET specific surface area ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	Microporous pore volume ($cm^3 g^{-1}$)	Average pore diameter (nm)
AC	2000 ± 90	1.35 ± 0.10	0.54 ± 0.05	2.1 ± 0.1
MAC	1950 ± 60	1.32 ± 0.08	0.52 ± 0.03	2.2 ± 0.07

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