

Efficient adsorption of benzoic acid from aqueous solution by nitrogen-containing activated carbon

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ABSTRACT

Adsorption is an efficient treatment process to remove benzoic acid from aqueous solution. In this study, nitrogen-containing surface groups were introduced onto activated carbon (AC) surface by modification with ammonium hydroxide, ammonium carbonate, melamine or urea. The nitrogen-containing AC samples were characterized using N₂ adsorption-desorption, Boehm titration, determination of the pH of the point of zero charge (pH_{pzc}) and X-ray photoelectron spectroscopy. The adsorption of benzoic acid from aqueous solution by nitrogen-containing AC has been studied. The Langmuir model fitted the experimental data of equilibrium isotherms better than the Freundlich model. At initial solution pH 2.1, the adsorption capacity was closely related with the amount of pyridinic and pyrrolic N on the AC surface, which indicated these two nitrogen-containing groups played an important part in the adsorption process. The enhancement of adsorption capacity was due to the strengthened π - π dispersion force between benzoic acid and the AC basal plane. Since the surface charge of AC as well as the existence form of benzoic acid varied with solution pH value, the adsorption capacity was found to be highest at pH 3.8 and dropped sharply at higher or lower pH values.

Key words | activated carbon, adsorption, benzoic acid, nitrogen-containing functional groups

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INTRODUCTION

Benzoic acid is well known to be widely used as a food preservative and reaction intermediate (Xin *et al.* 2011). Benzoic acid-containing wastewater discharged from processes of manufacture and application is highly toxic, harmful and difficult to treat directly by the conventional biological treatment methods due to its low biodegradability. Treatment approaches, such as biological treatment (Pariente *et al.* 2008), photocatalytic degradation (Mehrotra *et al.* 2005) and chemical treatment (Koh & Nakajima 2000; Yang *et al.* 2010) have been extensively investigated in the treatment of benzoic acid from aqueous solution. Among them, adsorption is an effective technology for removal of benzoic acid from wastewater or other aqueous solutions (Chern & Chien 2001; Ayranci *et al.* 2005).

Activated carbon (AC) is an attractive adsorbent due to its high specific surface area, well-developed internal pore structure and abundant surface functional groups (Derylo-Marczewska *et al.* 2004). However, a significant drawback of activated carbon adsorption, presenting a low level of selectivity and adsorption capacity, was

revealed by several studies. Consequently, extensive studies have focused on the surface modification of activated carbon so as to improve its adsorption capacity. The acid treatment of AC affected its capacity to adsorb phenol, which was attributed to the significant effect on the surface functional groups rather than the surface area of AC (Cañizares *et al.* 2006). Similarly, acid treatment improved the adsorption property of methyl mercaptan on activated carbon when compared with the untreated AC. Hydrogen bonding between acidic groups formed by acid-treatment and thiol groups of methyl mercaptan played an important role in the adsorption of methyl mercaptan on AC (Tamai *et al.* 2006). Besides, the surface modification of the activated carbon using ammonia was shown to be able to enhance its adsorption capacity for 2,4-dichlorophenol (Shaarani & Hameed 2011) and 4-nitrophenol (Derylo-Marczewska *et al.* 2008). The enhancement of adsorption capacity was closely correlated with the increase in concentration of basic surface groups on the AC surface.

Actually, nitrogen-containing AC has been developed to remove heavy metals (Shang *et al.* 2014) and organic compounds (Qin *et al.* 2014, 2015; Yang *et al.* 2014; Qin & Chen 2016) from aqueous media. The nitrogen-containing functional groups were introduced onto the AC surface, which increased the adsorption capacity, selectivity and removal efficiency of heavy metals and organic pollutants due to the strengthened π - π dispersion force as well as the coordination of surface functional groups (Yang *et al.* 2014). However, few studies have investigated the effect of nitrogen-containing functional groups on the adsorption capacity of benzoic acid from aqueous solution.

In the present work, AC samples were modified with ammonium hydroxide, ammonium carbonate, melamine or urea to introduce the nitrogen-containing functional groups onto the AC surface, respectively. AC samples before and after modification were characterized using N₂ adsorption-desorption, Boehm titration, determination of the pH of the point of zero charge (pH_{pzc}) and X-ray photoelectron spectroscopy (XPS). The isotherm data for adsorption of benzoic acid were fitted with the Langmuir and Freundlich models. The effects of the porous property, acid-base property and nitrogen-containing functional groups on the adsorption capacity of AC were investigated. The possible mechanisms of the adsorption process and benzoic acid interactions with the AC surface were analyzed.

EXPERIMENTAL

Materials

The original AC (Ningxia Huahui Activated Carbon Co., Ltd, China), designated as ACP, was crushed and sieved to 16–40 mesh. It was treated with ammonium hydroxide, ammonium carbonate, melamine or urea at room temperature and ambient pressure according to the procedure proposed by Rivera-Utrilla & Sanchez-Polo (2004). For this purpose, 20 g of AC was placed in a round-bottomed flask with 100 mL of 20 wt.% nitrogen-containing reagents. The contact was maintained during 30 min under ultrasonic treatment. Then, the carbon residue was filtered, dried in an oven at 110 °C for 24 h and calcined in a tube furnace under a flow of Ar for 3 h at 600 °C, with a heating rate of 10 °C/min. Finally, the samples were cooled to room temperature and stored in a desiccator until their use. The resulting samples were denoted as ACN, ACC, ACM and ACU, relating the used nitrogen-containing reagents ammonium hydroxide, ammonium carbonate, melamine

and urea, respectively. All other chemicals required in the experiments were of analytical grade. Solutions were prepared by appropriate dilution with deionized water.

Characterization of AC

The specific Brunauer–Emmett–Teller (BET) surface area and pore volume of AC samples were determined from the adsorption and desorption isotherms of N₂ at –196 °C using a Builder SSA-420 instrument. The samples were out-gassed overnight at 300 °C in a vacuum environment prior to the adsorption measurement.

Boehm titration was conducted to determine the number and type of surface oxygen groups (Salame & Bandosz 2001). The pH of the point of zero charge (pH_{pzc}) was determined by the pH drift method according to the procedure proposed by Yang *et al.* (2014). In brief, 50 mL of a 0.01 mol/L KNO₃ solution was adjusted to successive initial values (pH_{initial}) between 2 and 12, by adding either HNO₃ or KOH. After 0.15 g AC was added into a 100 mL conical flask, the dissolved CO₂ was degassed by N₂ stripping. Then the conical flask was sealed using a rubber stopper and placed in a thermostat shaker with constant stirring. The final pH, reached after about 48 h, was noted as pH_{final}. The pH_{pzc} is the point when pH_{initial} was equal to pH_{final}.

XPS measurements were performed with a Kratos XSAM800 using an Al K α (1,486.6 eV, anode operating at 12 kV and 15 mA) radiation source. The binding energies were calibrated based on the graphite C 1s peak at 284.5 eV. XPS data corresponding to N 1s spectra were fitted using the software CasaXPS.

Adsorption experiments

Adsorption kinetic experiments were performed as follows: 0.10 g of adsorbents and 50 mL of 1,000 mg/L benzoic acid solution were placed in a conical flask. The flask was sealed and shaken at 200 rpm in a thermostat shaker maintained at 20 °C. The samples were periodically withdrawn and immediately filtered with 0.45 μ m membrane for further analysis. The concentration of benzoic acid was determined by spectroscopic measurement at wavelengths of 225 nm using a Unico-UV-Vis spectrophotometer UV-2000. The adsorbed amounts of benzoic acid (q_t , mg/L) at different intervals were calculated by the following equation:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

where q_t (mg/g) is the amount of uptake capacity at time t ; C_0 (mg/L) is the initial solution concentration; C_t (mg/L) is the solution concentration at time t ; m (g) is the mass of activated carbon and V (L) is the volume of the solution.

To determine the adsorption isotherms, 0.10 g of adsorbents was placed in a series of conical flasks containing different concentrations (100–1,000 mg/L) of 50 mL solution of benzoic acid. To ensure benzoic acid was completely in molecular form and the surfaces of all AC samples were positively charged, the initial pH of the solution was adjusted to 2.1 using 0.1 mol/L HCl solution. The flasks were shaken at 200 rpm for 24 h at 20 °C to attain equilibrium. When reaching equilibrium, the benzoic acid solution was separated from the adsorbent for further analysis. The amount of uptake capacity at equilibrium (q_e , mg/L) was calculated by Equation (2).

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where q_e (mg/g) is the amount of uptake capacity at equilibrium; C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of the solution, respectively; m (g) is the mass of activated carbon and V (L) is the volume of the solution.

The effect of solution initial pH on benzoic acid adsorption was studied at a pH range of 2–12 at 20 °C. The pH of the solution was carefully adjusted by adding 0.1 mol/L HCl or 0.1 mol/L NaOH solution and was monitored by a PHC-3C pH meter. The benzoic acid concentration was fixed at 1,000 mg/L and the dosage of activated carbon was 0.10 g.

RESULTS AND DISCUSSION

Textural and chemical characterization of AC

Table 1 displays the results of the textural properties of AC samples before and after modification. The original

Table 1 | Porous properties of AC before and after modification

Samples	S_{BET} (m ² /g)	V_t (cm ³ /g)	V_{micro} (cm ³ /g)	V_{meso} (cm ³ /g)	Mesopore fraction (%)
ACP	1,318	1.12	0.39	0.73	65.2
ACN	1,288	1.04	0.46	0.58	55.8
ACC	1,272	1.08	0.45	0.63	58.3
ACM	1,436	1.42	0.48	0.94	66.2
ACU	1,495	1.54	0.52	0.92	59.7

activated carbon (ACP) was a highly mesoporous carbon with large specific surface area (S_{BET} , 1,218 m²/g), pore volume (V_t , 1.12 cm³/g) and high percentage of a mesoporous structure (34.8% for V_{micro} and 65.2% for V_{meso}). It was noted that no major change was observed in pore structure after modification by ammonium hydroxide or ammonium carbonate. Nevertheless, the specific surface area (S_{BET}) and total pore volume (V_t) of ACM and ACU slightly increased, which may be due to the decomposition of melamine or urea during the treatment into highly reactive nitrogenating agents, which could attack the activated carbon and gasify it (Rivera-Utrilla & Sanchez-Polo 2004).

The results obtained from Boehm titration as well as pH_{pzc} are presented in Table 2. The results indicated that the treatment of ACP with N-containing agents produced an obvious change in the surface character. Whereas ACP showed an acidic character, the treated samples were basic, especially ACM (pH_{pzc} = 8.85). In addition, a noticeable increase was observed in the concentration of total base of all treated carbons because of the transformation of carboxylic, lactonic and phenolic groups into ammonium carboxylate. These results were confirmed by the pH_{pzc} that was changed from 6.24 to 7.82 for ACN, 8.34 for ACC, 8.85 for ACM and 8.58 for ACU. The nitrogen-containing basic groups were introduced onto the AC surface by modification.

The deconvolution of the XPS spectra corresponding to the N 1s region of the carbons was carried out following the procedure proposed by several authors (Raymundo-Pinero et al. 2002; Rivera-Utrilla & Sanchez-Polo 2004). As shown in Figure 1, the N 1s was deconvoluted into four different types of N-containing species: pyridine (N1, 398.5–398.8 eV), imine/amide/amine (N2, 399.9–400.2 eV), pyrrole (N3, 401.4–401.6 eV) and N-oxide (N4, 403.7–404.2 eV). A quantitative analysis was performed based on the XPS spectra. The surface atomic concentrations of C, O and N are summarized in Table 3. According to the XPS results, the treatment of ACP with the nitrogen-containing

Table 2 | Surface groups from the Boehm titration and pH_{pzc} of activated carbon

AC	Carboxy (meq/g)	Lactonic (meq/g)	Phenolic (meq/g)	Total acid (meq/g)	Total base (meq/g)	pH_{pzc}
ACP	0.364	0.412	0.182	0.958	0	6.24
ACN	0.352	0.289	0.255	0.896	0.214	7.82
ACC	0.204	0.296	0.294	0.794	0.246	8.34
ACM	0.216	0.242	0.127	0.585	0.306	8.85
ACU	0.228	0.254	0.134	0.616	0.282	8.58

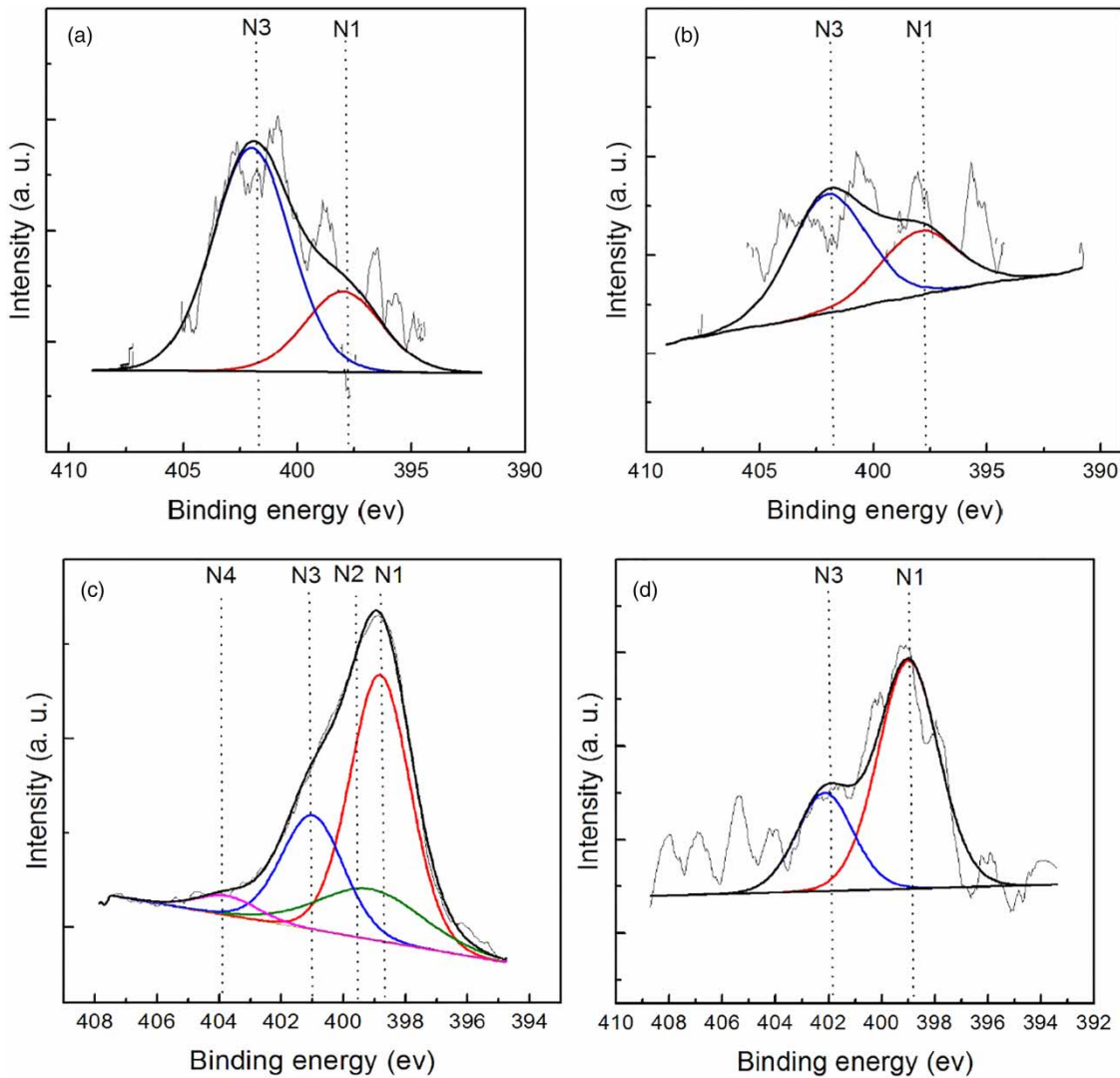


Figure 1 | Experimental and fitted N 1s XPS spectra of the samples (a) ACN, (b) ACC, (c) ACM and (d) ACU.

Table 3 | Atomic percentage of the elements on the AC surface measured by XPS

AC	C (%)	O (%)	N _{total}	N (%)			
				N1	N2	N3	N4
ACP	90.18	9.82	0	–	–	–	–
ACN	89.36	9.62	1.02	0.36	0	0.66	0
ACC	87.88	10.92	1.20	0.32	0	0.88	0
ACM	87.85	8.55	3.80	2.05	0.68	0.91	0.15
ACU	87.39	10.36	2.25	1.60	0	0.65	0

reagents reduced their C content because they introduced groups composed of N, H or O. The highest content of total nitrogen (3.80%) was observed in ACM. Moreover, N1 and N3 species were formed on the surface of all modified

AC samples, while N2 and N4 species only appeared on the ACM surface.

Adsorption kinetics of benzoic acid

In this study, the pseudo-first-order kinetic model and the pseudo-second-order model were used to investigate the adsorption of benzoic acid. The pseudo-first-order kinetic model is described in Equation (3). When $\ln(q_e - q_t)$ was plotted against time t , data fitted a straight line and k_1 and q_e corresponded to the slope and intercept of the line, respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where q_e and q_t (mg/g) are the amount of benzoic acid adsorbed at equilibrium and at time t , respectively; k_1 (1/h) is the first-order rate constant.

The pseudo-second-order kinetic model is described in Equation (4). The plot of t/q_t against t should give a linear relationship. The rate constants k_2 and adsorption capacity at equilibrium q_e were calculated from the values of the slopes and the intercepts.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where q_e and q_t (mg/g) are the amount of benzoic acid adsorbed at equilibrium and at time t , respectively; k_2 (g/mg.h) is the second-order rate constant.

The parameters of the pseudo-first-order kinetic model and pseudo-second-order kinetic model for AC samples were calculated and are listed in Table 4. The theoretical uptakes $q_{e, cal}$ were departed from the experimental values $q_{e, exp}$ and all correlation coefficients R^2 were smaller than 0.96, indicating that the pseudo-first-order equation was ruled out from describing the kinetics of the adsorption.

However, all the correlation coefficients R^2 for the pseudo-second-order kinetic model were above 0.99. Moreover, the theoretical uptakes $q_{e, cal}$ were in good agreement with the experimental uptakes $q_{e, exp}$ for the pseudo-second-order expression. These results indicated that the pseudo-second-order kinetic model was the suitable equation to describe the adsorption kinetics of benzoic acid on AC. The second-order rate constant for ACP was 0.00182 g/mg.h. In the present of ACM, the adsorption rate constant of benzoic acid enhanced more than 25% compared to ACP.

Adsorption isotherms of benzoic acid

Equilibrium adsorption isotherms are important to describe how the adsorbate will interact with the adsorbent. To

ensure benzoic acid was completely in molecular form and the surface of all AC samples was positively charged, the initial pH of the solution was adjusted to 2.1. The adsorption isotherms of benzoic acid on AC samples at 20 °C are compared in Figure 2. The experimental data were fitted with the Langmuir and Freundlich models. The Langmuir equation and Freundlich equation were formulated as Equations (5) and (6), respectively.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where q_m (mg/g) is the maximum adsorption capacity to form a complete monolayer on the surface of adsorbate; K_L (L/mg) is the Langmuir constant.

$$q_e = K_F C_e^{1/n} \quad (6)$$

where K_F ((mg/g)(mg/L)^{-1/n}) is the Freundlich constant that represents the quantity of adsorbate adsorbed onto the adsorbent for a unit equilibrium concentration; n is the dimensionless exponent of the Freundlich equation depicting an indication of how favorable the adsorption process is.

The parameters of Langmuir and Freundlich models are listed in Table 5. The correlation coefficient (R^2) was greater than 0.987 in the Langmuir model, suggesting that the Langmuir model fitted well to the data. Comparing the fitted curves in Figure 2 and the R^2 values listed in Table 5, the Langmuir model fitted the benzoic acid adsorption equilibrium data better than Freundlich model. Similar results were reported by other authors (Chai & Ji 2012).

It can be observed from Table 5 that the adsorption capacity of AC was improved by introducing nitrogen-containing functional groups onto the AC surface. ACM showed the highest adsorption capacity of 363.40 mg/g, increasing more than 15% compared to the original ACP. The values of q_m indicated that the adsorption capacity of

Table 4 | Parameters of the pseudo-first-order kinetic model and pseudo-second-order kinetic model for adsorption of benzoic acid on AC at 20 °C

AC	$q_{e, exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		$q_{e, cal}$ (mg/g)	k_1 (1/h)	R^2	$q_{e, cal}$ (mg/g)	k_2 (g/mg.h)	R^2
ACP	289.56	223.45	0.0268	0.928	298.76	0.00182	0.998
ACN	301.28	238.56	0.0274	0.958	305.12	0.00189	0.996
ACC	305.24	241.66	0.0281	0.886	308.64	0.00195	0.999
ACM	341.22	256.28	0.0312	0.956	342.56	0.00228	0.998
ACU	316.58	272.34	0.0305	0.925	321.45	0.00212	0.998

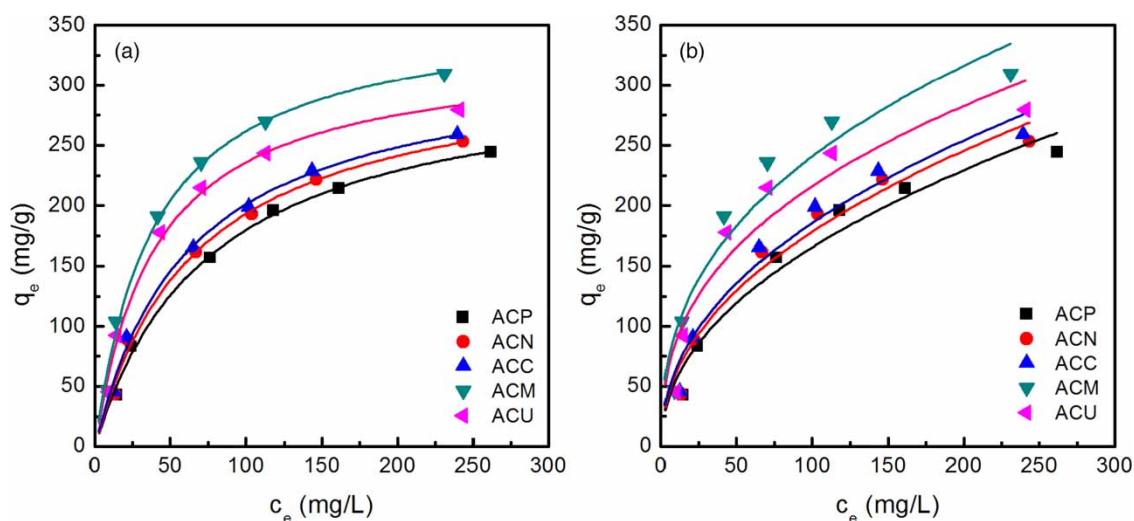


Figure 2 | Langmuir (a) and Freundlich (b) adsorption isotherms for benzoic acid on AC at 20 °C and pH 2.1.

Table 5 | Langmuir and Freundlich parameters for the adsorption of benzoic acid on AC samples

AC	Langmuir model			Freundlich model		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F ((mg/g) (mg/L) $^{-1/n}$)	n	R^2
ACP	315.12	0.013	0.995	19.01	2.13	0.947
ACN	320.72	0.015	0.993	21.48	2.17	0.948
ACC	324.71	0.016	0.994	23.21	2.21	0.949
ACM	363.40	0.026	0.988	39.55	2.59	0.899
ACU	330.09	0.025	0.987	36.56	2.55	0.881

AC samples increased in the order ACP < CAN < ACC < ACU < ACM. It was noted that there was no linear relation between the adsorption capacity and S_{BET} (Table 1), suggesting the nitrogen-containing functional groups introduced by modification played an important role in the adsorption of benzoic acid. Therefore, it was significant to investigate the effect of nitrogen-containing groups in the adsorption of benzoic acid.

Effect of nitrogen-containing functional groups on benzoic acid adsorption

It was known that the adsorption capacity depended on surface areas, so a parameter q_m/S_{BET} was used to correct the adsorption capacity for the surface areas of AC samples so as to investigate the contribution of different nitrogen-containing groups to the enhancement of adsorption capacity. A linear equation is used to fit q_m/S_{BET} and the

amount of nitrogen-containing functional groups (N1 + N3). The results were presented in Figure 3. The correlation coefficient (R^2) between q_m/S_{BET} and the amount of (N1 + N3) was above 0.97, indicating the adsorption capacity was closely related with these two groups. Therefore, pyridinic and pyrrolic N groups were the major nitrogen-containing species for the enhancement of adsorption capacity of AC.

Actually, the types of interactions between the carbon surface and the adsorbate were considered to be electrostatic attraction and dispersion interactions between π electrons of benzoic acid and π electrons in basal plane of AC (Nevskaia et al. 1999). In the adsorption conditions of

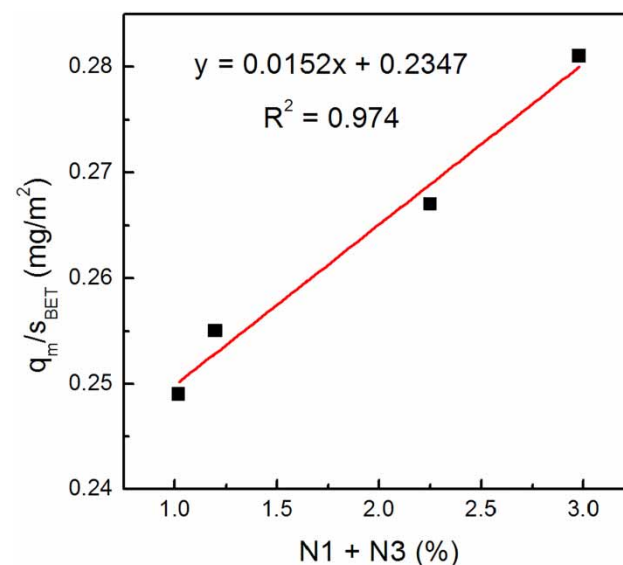


Figure 3 | Correlation between q_m/S_{BET} and amount of (N1 + N3) at 20 °C.

Table 5 (pH = 2.1), benzoic acid was mainly in neutral molecular type. Therefore, the π - π dispersive interactions between benzoic acid and AC basal plane predominated. As presented in **Figure 4**, nitrogen atoms in the pyridinic and pyrrolic groups on the nitrogen-containing AC supplied their p -electrons to the system of π -conjugated ring, so AC samples with pyridinic and pyrrolic groups showed higher electron density (Strelko *et al.* 2000). As a result, the π - π dispersion force between benzoic acid and the basal plane of AC was strengthened, thus more benzoic acid molecules were adsorbed on the surface of nitrogen-containing AC.

Effect of initial pH on benzoic acid adsorption

Since the adsorption of benzoic acid by AC was strongly initial pH dependent, the adsorption of benzoic acid at different initial pH (2.1, 3.8, 5.8, 8.1 and 10.2) by AC was investigated and the results are illustrated in **Figure 5**. It was observed that a similar trend of pH effect was observed for the adsorption of benzoic acid on all AC samples. The adsorption amount of benzoic acid was the highest at the initial pH of 3.8 and decreased sharply at higher or lower initial pH values. In addition, a lowest adsorption capacity of about 145 mg/g was observed at pH 10.2 for all AC samples.

It is known that at pH values lower than pH_{pzc} the surface is positively charged (Nevskaia *et al.* 1999). For example, since pH_{pzc} for the original ACP was 6.24, the carbon surface was positively charged below this pH value. On the other hand, benzoic acid was mainly neutral molecular in acidic solution and benzoic acid molecules

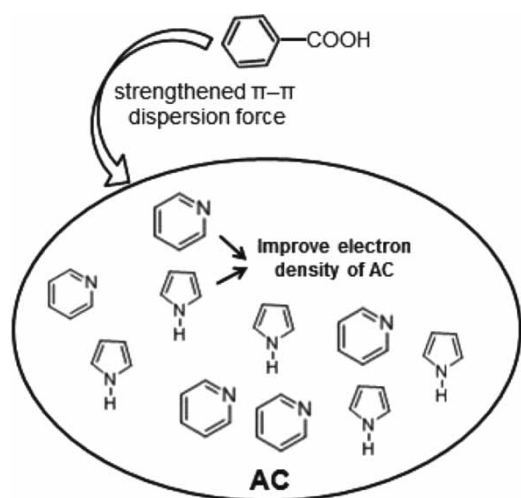


Figure 4 | The role of (N1 + N3) in the adsorption of benzoic acid by N-doped AC.

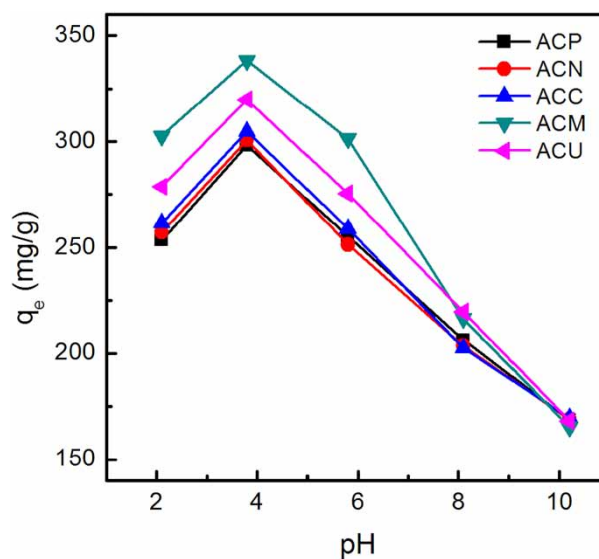


Figure 5 | Effect of initial pH on benzoic acid adsorption by AC at 20 °C and the initial benzoic acid concentration of 500 mg/L.

started to dissociate into benzoate anions as the initial pH increased. At initial pH 2.1, the undissociated species of benzoic acid were high and the main interaction between the AC surface and benzoic acid was expected to be dispersion interactions between π electrons of benzoic acid and π electrons in the basal plane of the AC. At initial pH 3.8, the AC surface was positively charged and benzoic acid (pK_a : 4.2) was dissociated to benzoate anions. The type of interaction between the surface and the adsorbate was electrostatic attraction, which explained the greatest adsorption capacity observed at this initial pH. At initial pH 5.8, although the benzoic acid was almost completely in anionic benzoate form, due to the decrease in surface positive charge compared to that at pH 3.8, there was an apparent decrease in the extent of adsorption. The ACP and ACN surfaces were negatively charged at initial pH 8.1 and all AC surfaces were negatively charged when initial pH reached 10.2. Electrostatic repulsion between the benzoate anions and AC surface must be operative at these pH values leading to the adsorption capacity decreasing to a minimum value (Ayrançi *et al.* 2005).

CONCLUSIONS

Nitrogen-containing activated carbon, modified by four different nitrogen-containing reagents, significantly improved the adsorption capacity for benzoic acid and AC modified by melamine (ACM) showed the highest uptake.

The enhancement of adsorption capacity was attributed to the introduction of nitrogen-containing functional groups. Pyridinic and pyrrolic groups played an important role in the adsorption of benzoic acid. The free electrons in pyridinic and pyrrolic N species delocalized to the basal plane leading to strong interaction between the AC and benzoic acid. The adsorption capacity was found to be highest at pH 3.8 in the pH range from 2.0 to 11.0. The very small adsorption capacity observed at pH 8.1 and 10.2 was attributed to increased electrostatic repulsions between benzoate anion and the negative surface charge at these initial pH values. Nitrogen-containing AC was an effective adsorbent in the adsorption of benzoic acid. Therefore, it may have a prospective application in the treatment of benzoic acid-containing wastewater.

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