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Effect of basicity and hydrophobicity of amines on their adsorption onto charcoal

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ABSTRACT

Amines are toxic and precursors for highly toxic nitrosamines and chloramines. Two groups of aliphatic highly soluble amines (methylamine MA, glucosamine GA) and aromatic amines (benzylamine BA, aniline AN, diphenylamine DPA) with varying degree of basicity and hydrophobicity were investigated for their adsorption onto charcoal. The adsorption experiments were carried out at 25 and 80˚C close to the temperature used in water treatment and decolorization processes, respectively, in order to understand the efficiency of charcoal in removal of amine pollutants in these processes. The adsorption order at 25˚C was: BA (0.9) > MA (0.72) > AN (0.63) > DPA (0.48) > GA (0.30 mmol/g), and the order at 80˚C was BA > AN > GA ~ MA ~ DPA. Both the orders reflected the importance of basicity over hydrophobicity of amines in the adsorption onto charcoal. The charcoal was characterized using FTIR, SEM, elemental analysis, Boehm titration, pH titration, and pH drift methods. The charcoal was found to have significant amount of carboxylic, lactonic, and phenolic functional groups. The adsorption of amines onto charcoal was found to increase with increasing pH, which was interpreted in terms of a model that depends on acid–base reaction between basic amines and acidic functional groups of charcoal.

Keywords: Adsorption; Charcoal; Methylamine; Glucosamine; Benzylamine; Aniline; Diphenylamine

1. Introduction

This work deals with aromatic and aliphatic amines. Aromatic amines are an important class of environmental pollutants in water. They are highly toxic and suspected to be carcinogenic even at low concentrations [1]. These chemicals have been classified as priority pollutants by the US Environmental Protection Agency [2]. Due to their high toxicity and accumulation in the environment, aniline (AN) compounds have been identified as potential carcinogens that possess the ability of preventing oxygen uptake in the blood and thus causing damage to the spleen [3]. Diphenylamine (DPA) is included in the third European Union (EU) list of priority pollutants [4,5]. Furthermore, the *N*-nitroso derivatives of aromatic amines are potential carcinogenic agents [6].

Aromatic amines are widely used as raw materials or intermediates in the manufacturing of dyestuffs, rubbers, synthetic polymers, pesticides, surfactants, corrosion inhibitors, cosmetics, and pharmaceuticals [1,2,6,7]. In the dyeing producing process, a large quantity of high toxic wastewater is discharged, which contains AN and its derivatives [1]. AN is produced as a result of the biodegradation of certain azo dyes and herbicides (e.g. acylanilides, phenylureas, and phenyl carbamates) [3]. DPA is an agrochemical

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compound with high antioxidant properties widely employed to control storage scald on apples and pears and as an antioxidant in the rubber and elastomer industries [4,5].

On the other hand, according to the European Union risk assessment report (2008, Germany): “Aliphatic amines are classified as very toxic to the aquatic organisms. Many cause long term adverse effects in the aquatic environment” [8]. The major risk of adverse environmental or health effects of alphatic amines in surface waters is not from the aliphatic amines themselves but rather due to the potential for aqueous phase formation of carcinogenic compounds (with low concentrations as 0.2 ng/L) such as nitrosamines through reactions between aliphatic amines and oxidants such as nitrite (NO_2^-) [7,9,10]. Furthermore, chlorination of water containing amines gives toxic chloramines which cause bad odor and taste of drinking water [11].

The sources of aliphatic amines in the environment are continuously increasing. Alkyl amines are used in floatation of halides, silicates, and zinc ores. The potassium salts of alkyl amines are used as soil fertilizers in agriculture. Furthermore, due to their water repelling properties, acetate and stearyl salts of hydrogenated tallow (triglycerides) amine are used in the potash and fertilizer industries as anticaking agents. They prevent caking during storage and transport, maintaining flowability of potash and fertilizers in crystal or granule form. As a result of these applications, amines are released into the surface water and agricultural soil [8]. Amine-based post-combustion CO_2 capture technologies, may present a new and significant source of amines to the environment [10,12]. Examples for amines used in CO_2 capture are monoethanolamine, diethanolamine, and N-methyldiethanolamine. The degradation of alkanolamines is an important issue because it causes environmental problems [12]. The most prevalent and commonly detected amines in surface water were methylamine, dimethylamine, ethylamine, diethylamine, and monoethanolamine [10].

Charcoal consists of stacked, condensed, and highly disordered polycyclic aromatic sheets [13]. Charcoal is the oldest form of human-made carbon from carbonization of biomass [13,14]. Carbonization is heat treatment or pyrolytic decomposition of a heterogeneous precursor material like coal or wood in the absence of oxygen at 400–600˚C [13]. Charcoal was used as decolorizing agent in chemical and food industries and in gas masks [15].

Charcoal is the forerunner of activated carbon. The latter is broadly defined to include a wide range of amorphous carbon-based materials prepared in such a way that they exhibit a high degree of porosity and an extended surface area [15]. Activated carbon is made under special atmospheres and higher temperature than charcoal. Activated carbon (900–110 m^2/g) has higher specific surface area than charcoal (200–500 m^2/g) [13,14]. Nowadays, activated carbon finds wide applications in environmental field (removal of organic and inorganic pollutants from surface and ground water), decolorization of oils and fats, sugar refining, decaffeination of coffee, and removal of sulfur-containing toxic components from exhaust gases, biogas purification, and gas masks [15]. Decolorization process is usually carried out at elevated temperatures. For example, decolorization of sugar syrup with powdered activated carbon can be done using a batch process at a temperature between 80 and 90˚C [16].

According to the “CRC Handbook of Activated Carbon Adsorption”, the adsorption of molecules onto activated carbon decreases with increasing solubility, branching, and polarity of molecules. Substituents like hydroxyl and amino groups tend to decrease the adsorption of molecules onto activated carbon [17]. Groups of organics that are generally amenable to adsorption onto activated carbon includes (i) pesticides and herbicides, (ii) aromatic solvents, (iii) chlorinated aromatics, phenols, and chlorinated solvents, (iv) high molecular weight acids, amines, esters, ethers, alcohols, surfactants, and soluble organic dyes [15]. Compounds having low molecular weight and high polarity such as low molecular weight amines, glycols, and ethers are not amenable to adsorption onto activated carbon [15].

A limited number of studies were reported for adsorption of amines onto activated carbon. Rao et al. [18] studied the adsorption behavior of diphenylamine, beta-naphthylamine, alpha-naphthylamine, and aniline on activated carbon and found that the % adsorption was 100, 99, 100, and 15%, respectively [18]. For the purpose of capturing CO_2, Houshmand et al. studied grafting ethylenediamine and diethylenetriamine onto activated carbon (activated by HNO_3). The % N in the activated carbon was raised from 0.31 to 8.25% after refluxing activated carbon with ethylenediamine [19].

The nonpolar surface of activated carbon, resulted from manufacturing conditions at high temperature, accounts for the poor adsorption capacity toward polar water-soluble amines [20]. On the other hand, the charcoal carbonized at 400–500˚C was found to have significant amount of acidic functional groups on its surface and as a result it was effective for the adsorption of basic ammonia gas. The amount of ammonia gas adsorbed increased with treatment of charcoal with oxidizing agents [11]. Iyobe et al.

investigated the adsorption of ammonia, methylamine, dimethylamine, and trimethylamine gases onto woody charcoal carbonized at 500˚C and activated carbon. It was found that the high acidity of charcoal was more suitable for adsorption of ammonia and methylamine than activated carbon, although activated carbon has a much larger pore volume and surface area than charcoal [21]. Norit SA 2 commercial charcoal was selected in the present study as an adsorbent. This is a steam activated carbon made from peat which is commonly used in treatment of drinking water and it is cheaper than others [22,23]. Preliminary tests of this charcoal indicated high acidic site content.

The aim of the present work was to investigate the adsorption behavior of highly water-soluble aliphatic amines (methylamine, glucosamine) and hydrophobic aromatic amines (benzylamine, aniline, and diphenylamine) onto commercial charcoal and elucidate the mechanism of adsorption. The effect of structural variability on adsorption will be used to elucidate the mechanism of adsorption. The adsorption study will be carried out at 25 and 80˚C in order to understand the efficiency of charcoal in removing amine pollutants in water treatment and decolorization processes, respectively.

2. Experimental

2.1. Materials

Commercial activated charcoal (NORIT® SA 2, steam activated, made from peat) and D(+)glucosamine (GA) were obtained from Acros Organics. Methylamine (MA, 40%), benzylamine (BA), aniline (AN), and diphenylamine (DPA) were from Riedel-DeHaen (Germany).

Unless otherwise mentioned, the charcoal was used after soaking in deionized water for 24 h, followed by filtration and drying at 100˚C.

2.2. Characterization of charcoal

Elemental analysis of charcoal was carried out using Eurovector Model E.A.3000 instrument (Italy). FTIR analysis of charcoal was done using MAGNA-IR560 Nicolet spectrometer (USA). Samples were ground with KBr and compressed to make pellets for which the infrared spectra were recorded in the range 400–4,000 cm^{-1}. The SEM analysis was conducted using FEI Inspect F 50 instrument.

The oxygen groups on charcoal surface that has acidic or basic properties were determined by Boehm titration method [24]. The acidic sites were determined by mixing 0.20 g of charcoal with 25 ml of three different bases; 0.10 M NaOH, 0.10 M $NaHCO_3$, or 0.10 M Na_2CO_3 in 100-ml plastic containers which were sealed and shaken for 24 h. The solutions were then filtered and back titrated with 0.1 M HCl. The first titration gives the total acidic sites, the second gives the lactonic and carboxylic groups, and the third gives only the carboxylic groups. Similarly, the basic sites were determined by mixing 0.2 g of AC with 25 ml of 0.1 M HCl, the obtained solution after shaking for 24 h and filtration was back titrated with 0.1 M NaOH.

The pH titration curves of charcoal were obtained using 0.5 g of AC in 50 ml of deionized water. The pH of the mixture was measured using Jinway pH meter (UK) after addition of 1-ml increments of 0.025 M HCl solution.

The pH_{pzc} of charcoal (the pH above which the total surface of charcoal is negatively charged) was determined by the so-called pH drift method [25]. A 0.5-g sample of charcoal was stirred in closed plastic containers for 24 h with 25.0 ml of deionized water whose initial pH was adjusted between 2.0 and 11.0 with drops of NaOH and HCl solutions. The change in pH from initial to equilibrium values was recorded.

2.3. Spectrophotometric determination of amines

The amines studied in the present work were determined using ninhydrin method according to the work of Wu et al. [26]. A 2.0-ml sample was withdrawn (Eppendorf micropipette) into a test tube to which 2.0 ml of 0.8% ninhydrin was added, followed by 2.0 ml of phosphate buffer (0.2 M KH_2PO_4, pH 6). The test tubes were heated in a water bath (Memmert) for 30 min at 80˚C. The absorbance of the resulted colored solutions was measured using double beam UV–vis spectrophotometer (Jasco V-530) at 570 nm. This method was applied for all the investigated amines except AN and DPA which were determined by direct measurement of absorbance at 280 and 320 nm, respectively.

2.4. Adsorption isotherms of amines on charcoal at 250˚C

Stock solutions of MA, GA, BA, AN, and DPA were prepared by dissolving 0.500 g of amine sample in deionized water in 100-ml volumetric flask. Portions of different volumes of stock solution were pipetted into 50.0-ml volumetric flask and the pH was adjusted to the value of 7 before completely diluting it with deionized water to the marks. Each 50.0 ml of the solution was divided into two portions. The first 25.0-ml portion was shaken with 0.5 g of charcoal in sealed plastic bottles at 25˚C and 145 min^{-1} (Kuhner, Switzerland) for 24 h and the second 25-ml portion (standard) was shaken without charcoal. After 24 h, the solutions were filtered and the filtrate was analyzed for amine as described in Section 2.3. The equilibration time of 24 h was fixed in all experiments because, preliminary experiments indicate that equilibrium is attained after 24 h as shown in Fig. 1.

2.5. Adsorption of amines onto charcoal at 80˚C

A 0.100 g of amine sample was dissolved in deionized water in 50-ml volumetric flask and the pH was adjusted to the value of 7 before completely diluting it with deionized water to the mark. The solution was divided into two 25.0-ml portions. The first portion was heated in closed conical flask to 80˚C with 1.0 g of charcoal using electrical heater with magnetic stirrer, and the second portion (standard) was heated without charcoal. When the temperature of solutions reached 80˚C, the solutions were immediately filtered and then analyzed for amine as described in Section 2.3. It is worth mentioning that long-time heating was avoided in order to prevent evaporation of amines, and the standard solutions were heated to correct any evaporated amine.

2.6. Effect of pH on adsorption of amines onto charcoal

The stock solutions of amines were prepared by dissolving 0.5 g of amine in deionized water in 100-ml volumetric flasks. Portions of 10.0 ml of stock solution were pipetted into 50.0-ml volumetric flask and the pH was adjusted to pH values of 1, 2, 3, 4, 5, and 7 using drops of diluted HCl and NaOH solutions. Each 50.0 ml of the solution was divided into two portions. The first 25.0-ml portion was shaken with 0.50 g of charcoal in sealed plastic at 25˚C bottles for 24 h and the second 25-ml portion (standard) was shaken without charcoal. After 24 h, the solutions were filtered and the filtrates were analyzed for amines.

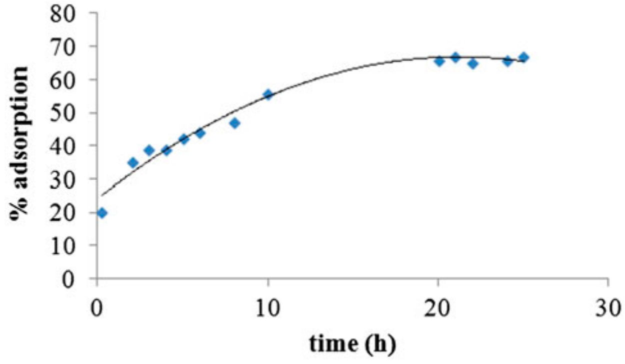

Fig. 1. The % adsorption of GA as a function of time.

Two models for interaction of amines with charcoal sites can be postulated for explaining the effect of pH on adsorption of amines onto charcoal. The first depends on acid–base reaction between the amine (RNH_2) and acidic functional groups (carboxylic or phenolic) of charcoal. The second depends on ion-exchange reaction of the ammonium form of amine (RNH_3^+) with sodium or potassium carboxylates or phenolates of charcoal. The first model was developed in the following paragraphs and second model was excluded due to evidences given in Sections 3.5 and 3.6.

The following equilibria are supposed to occur in the adsorption process:

(1) Dissociation of acidic sites of charcoal (C):

$$H_2C \leftrightarrow HC^- + H^+ \quad Ka1 \tag{1}$$

$$HC^- \leftrightarrow C^{2-} + H^+ \quad Ka2 \tag{2}$$

The first dissociation belongs to the relatively strong carboxylic sites, while the second belongs to the weak phenolic and lactonic sites of charcoal. The values of pK_{a1} (3.9) and pK_{a2} (11.9) were obtained from the work of Faur-Brasquet et al. [27], because the reported value of pH_{pzc} 9.53 is close to that of the present work (9.6).

(2) Dissociation of RNH_3^+ of the amine:

$$RNH_3^+ \leftrightarrow RNH_2 + H^+ \quad Ka \tag{3}$$

(3) Acid–base reaction between the amine (RNH_2) and acidic functional groups of charcoal.

$$RNH_2 + H_2C \leftrightarrow RNH_3^+ \cdot HC^- \quad Kr \tag{4}$$

where $RNH_3^+ \cdot HC^-$ is the surface reaction product and may represent an electrostatic interaction of the ammonium form of amine and negatively charged carboxylate and phenolate sites on charcoal.

The mass balance equation for the amine:

$$\text{The initial concentration of amine } C_{i,\text{amine}} = [RNH_2] + \left[RNH_3^+\right] + \left[RNH_3^+ \cdot HC^-\right] \tag{5}$$

The mass balance equation for charcoal:

$$\text{Concentration of acidic sites of charcoal } (C_T) = [H_2C] + [HC^-] + \left[C^{2-}\right] + \left[RNH_3^+ \cdot HC^-\right] \tag{6}$$

Substituting $[RNH_3^+]$ and $[RNH_2]$ in Eq. (5) using Eqs. (3) and (4), the following formula that related the initial concentration of amine (C_i, amine) to the amount adsorbed $[RNH_3^+{\cdot}HC^-]$ can be obtained:

$$[RNH_3^+ \cdot HC^-] = \frac{C_{i,amine}}{\frac{Ka+[H^+]}{Kr[H_2C]Ka} + 1} \tag{7}$$

The value of $[H_2C]$ was calculated from Eq. (8) by substituting $[HC^-]$ and $[C^{2-}]$ in Eq. (6) using Eqs. (1) and (2) and assuming that $[RNH_3^+{\cdot}HC^-]$ is negligible relative to the value of C_T (0.077 mol/L).

$$[H_2C] = \frac{C_T}{1 + \frac{Ka1}{[H^+]} + \frac{Ka1 \cdot Ka2}{[H^+]^2}} \tag{8}$$

2.7. Release of Na and K from charcoal

Different charcoal samples were subjected to adsorption of BA as an example for an aromatic amine and GA as an example for aromatic amines, and the sodium and potassium released into solution were simultaneously determined using flame photometer (Jinway).

2.8. Effect of ionic strength on adsorption of amines onto charcoal

The same procedure in Section 2.6 was followed but using 0.1 M NaCl instead of deionized water in preparing GA solutions.

3. Results and discussion

3.1. Characterization of charcoal

The total acidic groups of charcoal, determined by Boehm titrations, was found to be 1.86 mmol/g. The carboxylic, lactonic, and phenolic groups were 0.63, 0.88, and 0.35 mmol/g, respectively. On the other hand, the total of basic sites was 2.00 mmol/g. The total acidic sites of charcoal were in the range of that observed for other kinds of charcoal (1–5 mmol/g) [21,28] but higher than that of activated carbon (0.3–1.2 mmol/g) [21,24,29]. The same observation was obtained by Iyobe et al. [21] that charcoal is more functionalized than activated carbon because charcoal is prepared at lower temperature than activated carbon. The FTIR spectrum of charcoal (Fig. 2) showed major three broad bands centered at 3,450, 1,640, and 1,400 cm^{-1} assigned to O–H stretching, C=O/C=C stretching, and carboxylate stretching, respectively [25].

The elemental analysis of charcoal was found to be 72.34% C, 1.62% H, and 0% N, 26% O. If these values are compared with those reported for activated carbon (palm shell oxidized with HNO_3) 85.25% C, 1.51% H, 0.31% N, 6.26% O, and 6.66% ash [19], and steam activated carbon (steam activated coconut shell) 96.22% C, 0.42% H, 0.28% N, and 2.95% O [30], it is evident that charcoal used in the present work has relatively high oxygen functional groups than activated carbon. On the other hand, the SEM graph of charcoal (Fig. 3) revealed that it has much less nanopores than activated carbon [31].

The pH titration curves of charcoal with HCl are given in Fig. 4. The initial pH values of charcoal washed with deionized water and raw commercial (as received) charcoal were 9.36 and 9.76, respectively. The highly basic pH is due to the fact that the basic sites of charcoal (2.00 mmol/g) are higher than the acidic sites (1.86 mmol/g). When the titration curves of charcoal are compared with the titration curve of water (Fig. 4), it is clear that charcoal has significant buffering capacity toward added H^+. This buffering capacity vanished after addition of 15 ml of 0.025 M HCl solution. Since the mass of charcoal used in titration was 0.50 g, the estimated amount of H^+ absorbed by charcoal is (15 mL × 0.025 M/0.5 g charcoal) 0.75 mmol H^+/g charcoal. This value is lower than the total basic sites of charcoal determined by Boehm titration which is 2.00 mmol H^+/g charcoal. This difference is due to the fact that the basic sites are more effectively reached after longer time (24 h) in Boehm method than in potentiometric instant titration. This indicates that some of the basic sites are deeply buried in the pores and channels of charcoal. The nature of the basic sites in charcoal is most probably carboxylate and phenolate functional groups because there is no measureable amount of nitrogen in charcoal.

The pH_{pzc} of charcoal, determined by pH drift method, was found to be 9.6 as shown in Fig. 5. The pH_{pzc} is the pH above which the total surface of charcoal is negatively charged [23]. Since the pH range of the present adsorption study (1–7) lies below the pH_{pzc}, the surface of charcoal is neutral or positive.

3.2. Adsorption isotherms of amines onto charcoal at 250˚C

The adsorption isotherms of MA, GA, BA, AN, and DPA are given in Fig. 6. The values of adsorption capacity Q_{max} and K_L (Table 1) were determined from the slope and intercept of the plot of C_{eq}/Q_{eq} vs. C_{eq} using the linear form of Langmuir model (Eq. (9), Fig. 6) [25]:

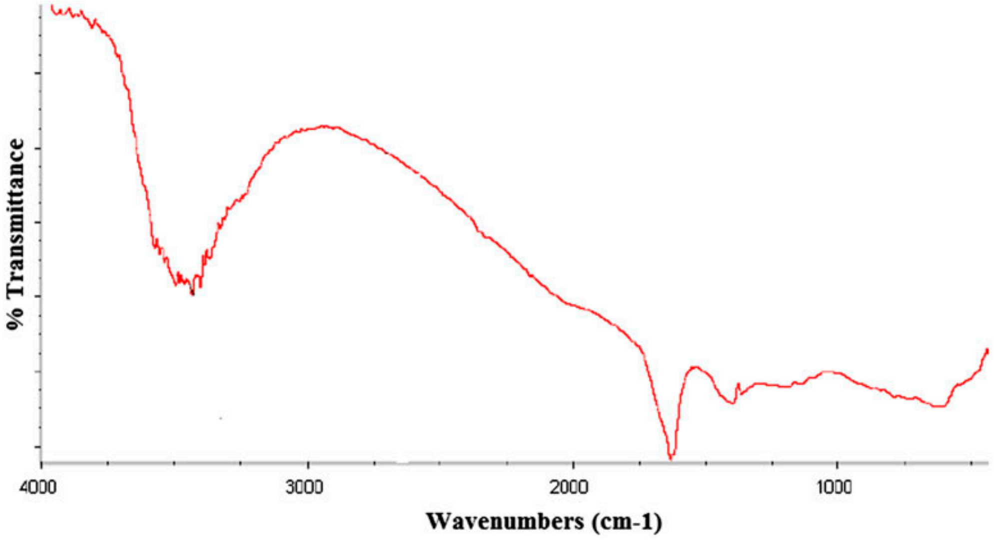

Fig. 2. FTIR spectrum of charcoal.

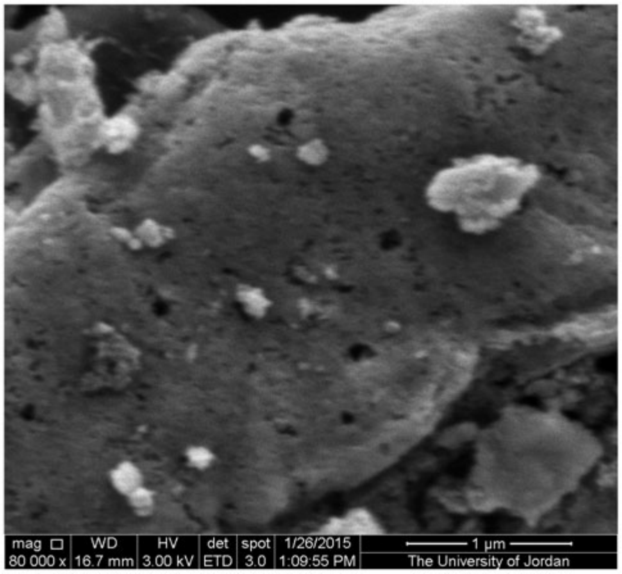

Fig. 3. SEM graph for charcoal.

$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{Q_{max}K} + \frac{C_{eq}}{Q_{max}} \tag{9}$$

where C_{eq} is the equilibrium concentration of amine (mmol amine/L), Q_{eq} is the amount of amine adsorbed onto charcoal (mmol amine/g charcoal), Q_{max} is the maximum amount of amine adsorbed or adsorption capacity (mmol amine/ g charcoal), and K_L is the affinity constant related to energy of adsorption.

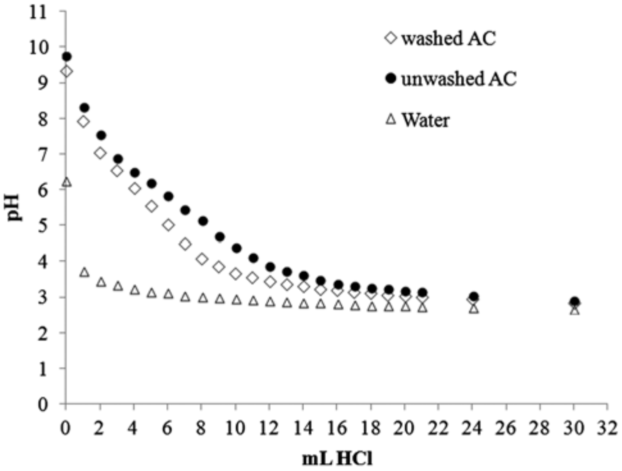

Fig. 4. The pH titration curve of 0.5 g charcoal in 50.0 ml of deionized water with 0.025 M HCl solution.

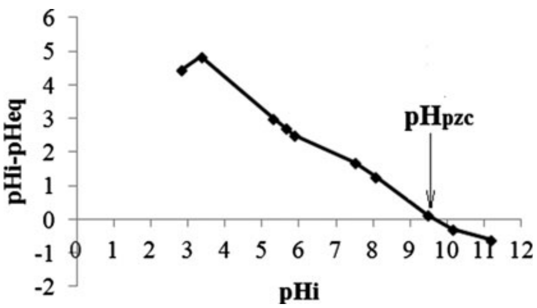

Fig. 5. The pH_{pzc} of charcoal determined by pH drift method.

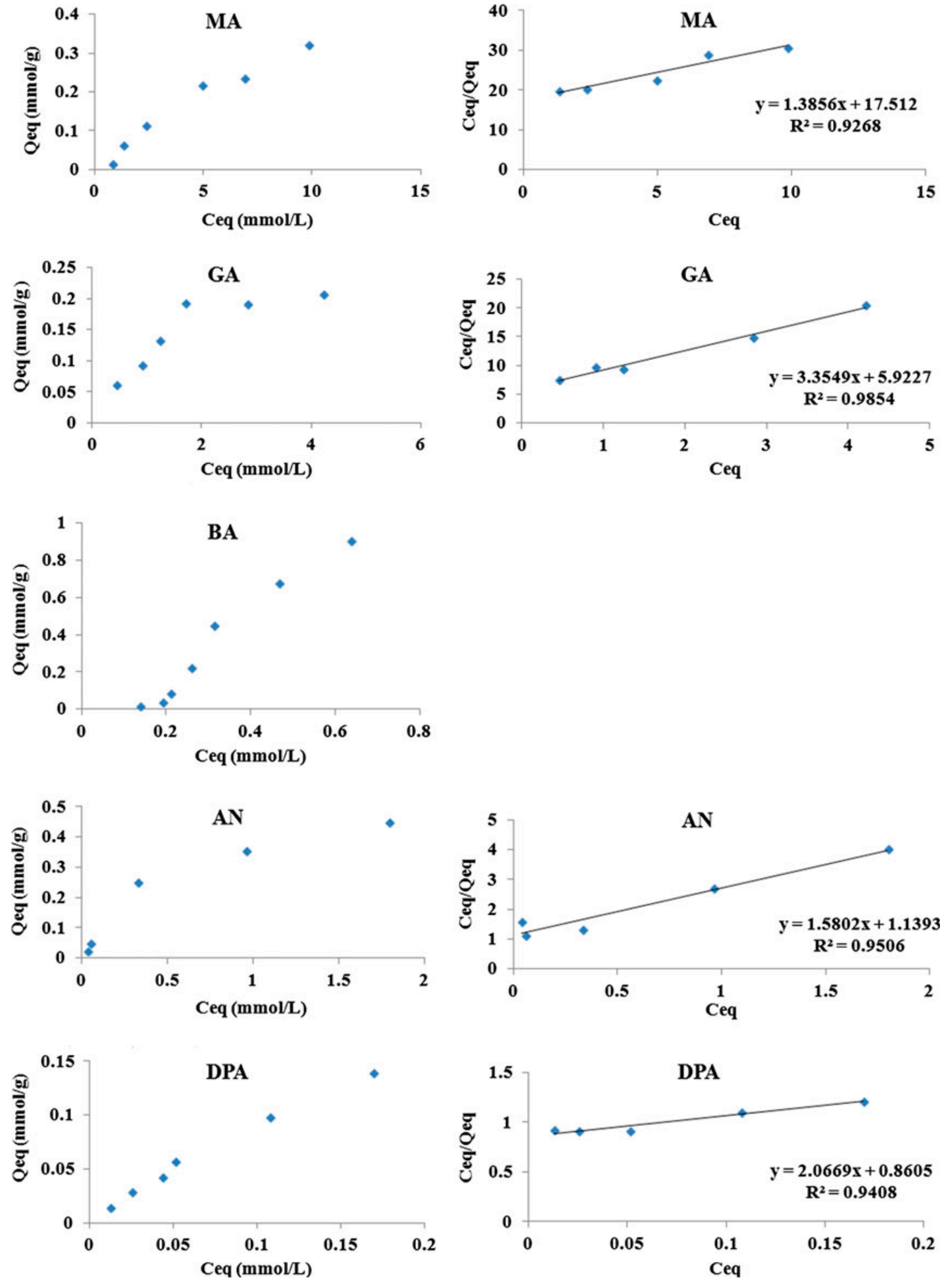

Fig. 6. Adsorption isotherms for amines onto charcoal.

In order to understand the relationship between the adsorption behavior and the properties of amines, the pK_a and octanol-water partition coefficient (K_{ow}) of amines studied are given in Table 1. The basicity of amine is inversely proportional to the pK_a value. K_{ow} provides a useful quantitative parameter for

Table 1
The maximum adsorption capacity (Q_{max}, mmol amine/g charcoal) of amines onto charcoal at 25˚C and pH 7

Amine	Q_{max}	K_L	R^2	pK_a [b]	$\log K_{ow}$ [b]
Methylamine (MA)	0.72	0.08	0.9268	10.65	−0.57
Glucosamine (GA)	0.30	0.57	0.9854	7.58	−4.2
Benzylamine (BA)	>0.90[a]	[a]	[a]	9.36	1.09
Aniline (AN)	0.63	1.39	0.9506	4.6	0.9
Diphenylamine (DPA)	0.48	2.40	0.9408	0.78	3.5

[a] The adsorption isotherm was not successfully fitted by Langmuir model.

[b] Values were obtained from Ref. [32].

representing the lipophilic/hydrophilic nature of amine [32], so the hydrophobicity of amine increases with an increase in the K_{ow} value.

Several mechanisms were proposed for adsorption of aromatic amines onto hydrophobic surfaces. The most important is hydrophobic interaction [23] and dispersion interaction between the π-electrons of aromatic ring of amine and those of the grapheme layer of carbon [33]. Depending on this mechanism, and depending on the values of K_{ow} (Table 1), the expected order of adsorption of aromatic amines onto charcoal should be DPA > BA > AN. However, depending on the Q_{max} values obtained in Table 1, the observed order was:

Q_{max}: BA (0.9) > AN (0.63) > DPA (0.48 mmol/g)
pK_a: 9.36 4.6 0.78

which is consistent with the order of basicity (pK_a in Table 1) of these compounds. This order indicated that the basicity of amines is more important than their hydrophobicity in the adsorption process.

The reverse of this order was reported by Rao et al. [18], where the adsorption DPA was stronger than AN on activated carbon. This difference may be due to the fact that the charcoal used in the present work has many acidic sites (less hydrophobic surface) than that of activated carbon. Furthermore, in the present work, BA, AN, and DPA were dissolved in 10% aqueous ethanol solution to ensure complete solubility of these aromatic amines, which may increase their solubility and thus affect mechanism of adsorption.

MA and GA are aliphatic amines with very low octanol-water partition coefficient (K_{ow}) as shown in Table 1. Although the highly water soluble MA and GA are expected to form strong hydrogen bonding with water and thus resist adsorption onto charcoal, they have relatively high values of adsorption capacity (Q_{max}). The adsorption capacity of MA, which has the highest basicity among the amines investigated, was greater than less basic GA and also greater than hydrophobic aromatic amines like DA and AN (Table 1).

In order to confirm the importance of the amine group in adsorption onto charcoal, glucose was tested for adsorption onto charcoal and compared with glucosamine. Glucose (Q_{max} 0.042 mmol/g) was much less strongly adsorbed than glucosamine (Q_{max} 0.30 mmol/g).

Several mechanisms for the adsorption of aliphatic alkyamines, cysteamine, and propylamine which were thought to be adsorb onto soil and Na-zeolite by cation exchange of the positively charged ammonium cations of these amines with sodium and potassium cations in the minerals [8,34]. The values of Q_{max} obtained for cysteamine and propylamine were 0.896 and 0.631 mmol/g, respectively [34], which are comparable with the values obtained for MA (0.72 mmol/g) in the present work. This cation-exchange mechanism will be investigated in Section 3.5. On the other hand, *n*-propylamine, *n*-hexylamine, diethylamine, and benzyl amine were reported to be adsorbed onto Na-montmorillonite by specific complex between donating amines and Na^+-montmorillonite ($RH_2N{:}\rightarrow Na^+$-montmorillonite) with an adsorption capacity of 0.88, 0.89, 0.52, and 1.15 mmol/g, respectively [35].

3.3. *Adsorption of amines onto charcoal at 80˚C temperature*

Adsorption experiments at 80˚C temperature were conducted in order to assess the efficiency of charcoal in removal of amines during decolorization processes of sugar syrups, vegetable oil, alcoholic beverages, and fruit juices which are usually carried out at 80–90˚C [16].

The results of adsorption of amines onto charcoal at 80˚C temperature were given in Table 2. In the case of aromatic amines, the highly basic BA has the strongest adsorption onto charcoal while the highly hydrophobic DPA was not adsorbed at all. The order of % adsorption at 80˚C was: BA > AN >> DPA which reflected the importance of basicity, rather than hydrophobicity as the driving force for adsorption. Interestingly, DPA which is an important agrochemical compound could not be removed during decolorization processes of sugar syrup, fruit juices, and beverage using charcoal at 80˚C.

In order to exclude the effect of adding ethanol to water (10% w/w) in dissolution of aromatic amines, L-phenylalanine which is similar in structure to BA and soluble in water, was studied and it was found that the % adsorption of L-phenylalanine (99.7) was high as in the case of BA (80.9%).

Highly soluble amines, like MA and GA were not adsorbed onto charcoal at 80˚C temperature. However, they were adsorbed at 25˚C with 24 h contact time which indicates that the highly soluble amines need long time in order to reach the acidic sites buried in the pores of charcoal.

3.4. Effect of pH on adsorption of amines onto charcoal

The effect of pH on the adsorption of MA and GA as examples of highly soluble aliphatic amines, and BA as an example of hydrophobic aromatic amine on charcoal are shown in Fig. 7. It is clear that the adsorption increases with increasing pH, which is in agreement with the reported increase in adsorption of aniline on Norti GCW carbon ($pH_{pzc} = 8$) from 0.48 mmol/g at pH 2 to 1.10 mmol/g at pH 11 [33]. This phenomenon can be ascribed, *prima facie*, to the reduction in competition of H^+ with the $R\text{-}NH_3^+$ toward the surface of charcoal with pH increase. However, this phenomenon will be investigated more deeply in the following paragraphs.

The pK_a values of MA, GA, and BA in Table 1 indicated that these amines are in the protonated $R\text{-}NH_3^+$ below the pH values of 10.65, 7.58, and 9.36, respectively. Furthermore, it was shown in Section 3.1 that the pH_{pzc} of charcoal is 9.6, which means that below this value, all the charcoal sites are in the positive or undissociated form. Thus, in the pH range of this study (pH 1–7), amines are in the protonated (positive) form and charcoal is in the positive or undissociated form.

Table 2
Adsorption of amines onto charcoal at 80˚C

Amine	% Adsorption
Methylamine (MA)	0.00
Glucosamine (GA)	4.5
Benzylamine (BA)	80.9
Aniline (AN)	51.1
Diphenylamine (DPA)	0.00

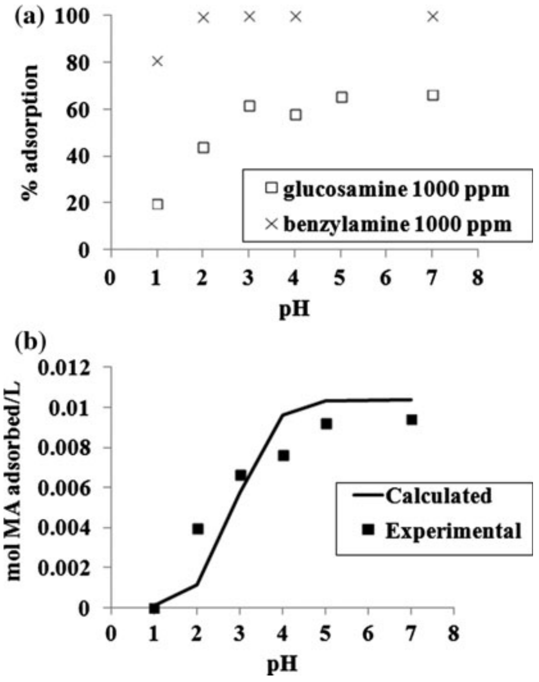

Fig. 7. (a) The effect of pH on the adsorption of GA and BA onto charcoal and (b) modeling the effect of pH on adsorption of MA onto charcoal.

Eq. (7) shows clearly that adsorption represented by $[RNH_3^+ \cdot HC^-]$ increases with increasing pH. MA ($C_{i,amine} = 0.0116$ M) with pK_a 10.65 [32] was selected to test the model because it gave high pH dependence. Eq. (7) was used to fit the pH-dependent data for MA. The solver of Microsoft Excel software was used to calculate the value of Kr (equilibrium constant for reaction of Eq. (4) that gives the minimum sum of square residuals between the calculated $[RNH_3^+ \cdot HC^-]$ (Eq. (7)) and experimental amounts of MA adsorbed. The model gave good description for the effect of pH on the adsorption of MA (Fig. 7(b)). The calculated Kr value was 6.2×10^8 (SSR = 1.52×10^{-5}). The large value of Kr accounts well for the highly favorable acid–base reaction postulated in Eq. (4).

3.5. Release of Na and K from charcoal

Since the elemental analysis of charcoal showed that there is no detectable nitrogen in charcoal, the basic sites of charcoal are expected to be sodium and potassium salts of carboxylates and phenolates. The present section investigated feasibility of ion-exchange model, i.e. the possibility that protonated amine (RNH_3^+) undergoes ion exchange with Na^+ and K^+ on the surface of charcoal.

Table 3
Leaching of Na and K from charcoal subjected to different treatments with amines

T#	Treatment	mmol Na/g charcoal	mmol K/g charcoal
1	25.0 ml of 10,000 ppm BA solution + 1.0 g charcoal at 80℃	0.026	0.017
2	25.0 ml of deionized water + 1.0 g charcoal at 80℃	0.015	0.018
3	25.0 ml of 1,000 ppm GA solution + 0.5 g charcoal at 25℃, 24 h shaking	0.019	0.014
4	25.0 ml of deionized water + 0.5 g charcoal at 25℃, 24 h shaking	0.014	0.011

A charcoal sample was subjected to adsorption of BA as an example for an aromatic amine at 80℃ (*T*#1, Table 3). The amounts of Na and K leached were compared to those leached from charcoal sample subjected to deionized water at the same temperature (reference, *T*#2, Table 3). Similarly, a charcoal sample was subjected to adsorption of GA as an example for an aliphatic amine at 25℃ (*T*#3, Table 3). The amounts of Na and K leached were compared to those leached from charcoal sample subjected to deionized water at 25℃ (reference, *T*#4, Table 3). A comparison between the amounts of Na and K released in the presence (*T*#1, 3) and absence (*T*#2, 4) of amines revealed that very small amounts of Na and K were released from charcoal during adsorption of amines. This leads to the exclusion of the ion-exchange model and thus favor of acid–base reaction model developed in the previous section. This is in spite of the finding (Section 3.1) that the number of ion-exchange basic sites in charcoal is higher than the acidic sites.

In order to test the stability of GA during adsorption experiments, a solution of GA was shaken with charcoal for 24 h at 25℃, and the solution was filtered and evaporated. The FTIR spectrum of the obtained solid was identical to that of standard GA which indicated that GA was not affected by contact with charcoal. The elemental analysis values of the same material were 26.63% C, 6.64% H, and 4.43% N which was close to the theoretical values of GA (33.4% C, 6.03% H, and 6.50% N) which support the observation that little amount of material is released from charcoal during adsorption.

3.6. Effect of ionic strength on adsorption of amines onto charcoal

If the adsorption of amines onto charcoal follows ion-exchange model, the process is expected to be sensitive to ionic strength. Increasing ionic strength of solution from $I = 0.0$ to 0.1 M NaCl (Fig. 8(a)) does not affect adsorption of GA on charcoal, which supports the idea that there is no ion exchange between the ammonium form of glucosamine and the sodium or carboxylates and phenolates on the surface of charcoal.

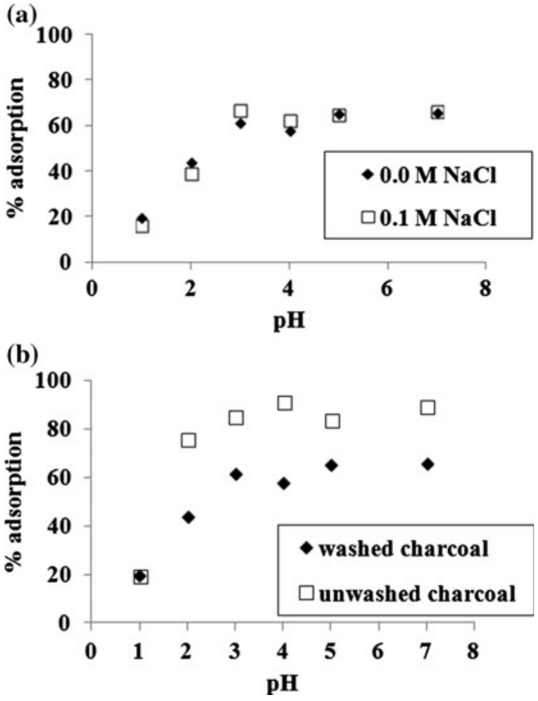

Fig. 8. (a) Effect of ionic strength on adsorption of GA onto charcoal and (b) comparison between the adsorption of GA onto washed and unwashed charcoal.

3.7. Effect of washing charcoal on adsorption of amines onto charcoal

The unwashed raw charcoal has been found to have somewhat stronger adsorption capacity toward glucosamine than washed charcoal (Fig. 8(b)). This is due to the fact that unwashed charcoal results in higher equilibrium pH of solution than washed charcoal (Fig. 4, Section 3.1). However, when the initial pH was adjusted to the value of 1, there was no difference between adsorption of glucosamine onto washed and unwashed charcoal (Fig. 8(b)).

4. Conclusion

In water treatment using charcoal, both water soluble and insoluble amines could be removed. However, in decolorization of sugar syrups, vegetable oil, alcoholic beverages, and fruit juices using charcoal at 80–90°C, basic and hydrophobic amines like benzylamine and aniline could be removed but not less basic diphenylamine. The highly hydrophobic diphenylamine is an agrochemical compound and may be present in the above food products and so it is a major concern that it will not be removed during decolorization.

Charcoal contains significant amount of acidic sites. The adsorption of amines onto charcoal increases with increasing basicity of amine and pH of solution, but is independent on ionic strength. Although the number of ion-exchange basic sites in charcoal is higher than the acidic sites, amines undergo adsorption onto charcoal by means of acid–base and not ion-exchange mechanism.

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