

Effect of Selected Parameters on Adsorption of Benzoic Acid on Activated Charcoal

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(Received 7th December, 2005, revised 26th January, 2006)

Summary: Benzoic acid was adsorbed on activated carbon under varying conditions such as time, pH and degassing temperature. Equilibrium adsorption was established within four hours. The pH was found to have considerable effect on adsorption. Increase in degassing temperatures had a significant effect on adsorption of benzoic acid. Various possible reasons for change in adsorption with pH and increase in degassing temperatures are discussed in details. Freundlich and Langmuir equations were successfully applied to the adsorption isotherm data of benzoic acid.

Introduction

The growing urbanization and industrialization is creating a variety of problems of human; pollution being the most serious one. Water pollution is a major cause of infant mortality and morbidity. Since water is essential for all living creatures, especially for human beings hence, contaminated drinking water has direct effect on humans while sewerage and industrial effluents, when used for irrigation purposes have indirect effect through consumption of crops, vegetables and fruits. According to World Health Organization (WHO) more than 80% human diseases are water borne. It is estimated that 30% of all the reported cases of illness and 40% of deaths in Pakistan are attributed to water borne diseases [1].

Now a day, the extensive use of organic compounds in industries like dyestuff, pharmaceuticals, pesticides, agriculture, tanning and dairy products are of growing concern for environmentalists due to their toxicity to aquatic system. Such type of polluted water needs to be purified before human consumption. Various techniques have been used for purification of polluted water but among these, the adsorption technique due to high rate, high uptake capacity, effective treatment in dilute solutions, low cost and regeneration claims as an honorable place [2-3]. Adsorption of organics from liquid phase by activated carbon has gained worldwide importance as a most effective way for the removal of trace organic compounds, which are usually present in ground and surface water. In a survey conducted in United States, more than seven hundred carcinogenic organic compounds were identified in drinking water [4].

The adsorption of organic compounds on surface of modified activated carbon was studied earlier [5-6]. Activated carbon is the most commonly used adsorbent for the treatment of water and wastewater due to its high adsorption capacity. Most of the water sources contain significant amount of toxic organic compounds [7]. Removal of these toxic organic compounds by treatment with activated carbon has gained widespread attention. Factors that are associated with the adsorbents are particle size, surface area, porosity and the amount and nature of chemisorbed oxygen. The role of granular activated carbon surface chemistry on the adsorption of trichloroethylene and trichlorobenzene was demonstrated [5-8]. Youru *et al.* [9] studied the adsorption of benzeoid and nonbenzeoid hydro-carbons on charcoal while Goworek *et al.* [10] observed the adsorption of benzene methanol mixture on carbon black modified with various sulfurizing substances. Bansal *et al.* [11] studied the adsorption of benzene on oxidized sugar charcoal. Both benzenoid and nonbenzeoid hydrocarbons including toxic organic compounds were adsorbed on activated carbon and Freundlich, Langmuir and IAS (Ideal adsorption solution) models were found to have good correlation in experimental and in calculated results [12]. Lankford [13] used powder activated carbon (PAC) for adsorption for toxic organic compounds. Ahmad *et al.* [14] adsorbed different organic acids on fly ash, activated charcoal and granular charcoal and found that adsorption of these acids obey Freundlich's equation. The dissolved oxygen effects on equilibrium and kinetics of benzoic acid adsorption were investigated [15]. Other parameters such as pore size [16], pH [5], surface physico-chemical characteristics [17] and

activity of different activated carbons [18]. Effect of surface modification of carbon on adsorption of organic compounds has been studied by earlier investigators [19] and it was observed that surface modification has a pronounced effect on adsorption. The pH is another important factor in determining the extent of adsorption of organic compounds. Effect of pH on adsorption of organics has been studied by earlier investigators [20].

Since, adsorption of organic compounds on carbon is influenced by the physico-chemical characteristics of the carbon surface, nature and concentration of the organic compound, pH, temperature, competing adsorbates etc. Therefore, the present work was therefore undertaken with a view to investigate the physico-chemical interaction of benzoic acid with the carbon surface and the role of surface functional groups on adsorption.

Results and Discussion

The standard calibration graph of benzoic acid is shown in Figure 1. The absorbance of the standard solutions was noted at a wavelength of 272.6 nm. The straight line of the graph shows the accuracy of the standard determinations in the concentration under study.

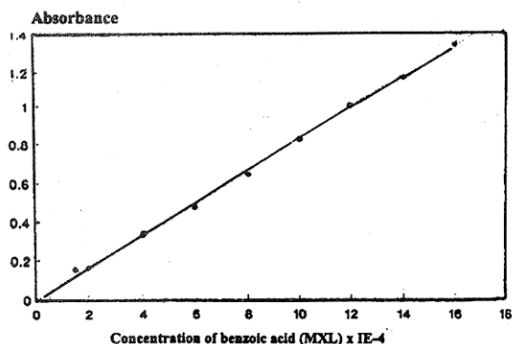


Fig. 1: Benzoic acid calibration curve.

The adsorption isotherms of benzoic acid on extracted sample in the molar concentration range from 1×10^{-3} to 1×10^{-2} M and the pH ranges 2.00–2.49, 3.60–4.44 and 8.46–8.88 are given in Figure 2. The isotherms indicate that the amount of benzoic acid adsorbed is quite high at low and intermediate pH compared to the amount adsorbed at high pH. High adsorption of benzoic acid at low and intermediate pH ranges may be due to the fact that at

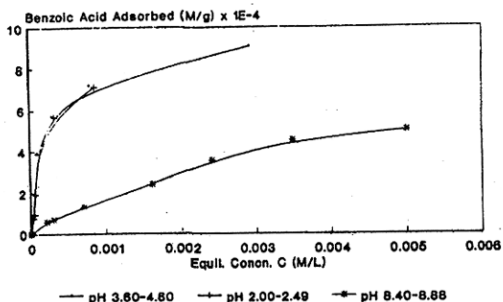
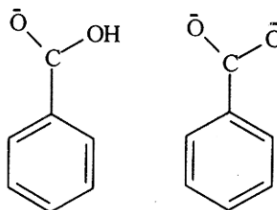
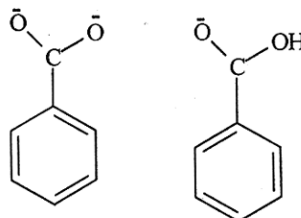


Fig. 2: Adsorption isotherms of benzoic acid on activated carbon (extracted) at different pH.

these pH ranges benzoic acid may not dissociate or partially dissociate into negatively charged benzoate and may be presented predominantly as neutral benzoic acid.



As the carbon surface is mostly composed of the non-polar basal plane area, therefore these neutral species might have adsorbed to a greater extent on the carbon surface. The non-polar fraction of the surface would have high affinity for the relatively non-polar undissociated benzoic acid species resulting in an increase in the adsorption of the benzoic acid at these pHs. At high pH benzoic acid is dissociated into negatively charged species as reported by Gould [21]



and the carbon surface acquires negative charge due to adsorption of hydroxyl amine, thus due to repulsion between the negatively charged carbon surface and benzoate anion, adsorption occurs to a

lesser extent at high pH range compared to low and intermediate pH ranges. A second reason for low adsorption at high pH might be due to the dissociation of oxygen functional groups into $-\text{COO}^-$ and $-\text{O}^-$ negatively charged species, which impart additional negative charge to carbon surface. Thus adsorption occurs to lesser extent at high pH due to repulsion between the negatively charged benzoate anion and the negatively charged carbon surface. Solubility of the adsorbate is an additional factor, which influence the adsorption i.e. hydrophobic substances will be more likely adsorbed from aqueous solution [22]. As solubility of benzoic acid is greater at high pH compared to low and intermediate pH. This result in lower adsorption at this pH compared to other two pHs. Yankic and Natarjan [23] reported that the most hydrophobic benzoic acid was adsorbed to a greater extent compared to other adsorbate due to comparatively lower solubility.

The adsorption isotherms of benzoic acid on activated carbon evacuated at 300 °C are given in Fig. 3. The molar concentration range varied from 2×10^{-3} to 2×10^{-2} M and pHs were 2.03-2.78, 3.10-4.78 and 8.29-8.86 respectively. The figure shows that the amount of benzoic acid adsorbed are comparatively high compared to the extracted samples at all the three pH ranges. This may be due to comparatively large surface area of evacuated sample compared to extracted sample which results in greater adsorption of benzoic acid as have been reported in case of phenol [24]. The lower adsorption of benzoic acid on extracted sample in addition to low surface area and may also be attributed to the fact that due to the surface functional groups a portion of carbon surface may be very polar which adsorbed water strongly though hydrogen bonding compared to non-polar organic compounds, which in turn would have reduced the adsorption capacity of benzoic acid by pore constriction or blocking mechanism, as reported by earlier workers for organic compounds [19, 25] and also noticed in the phenol adsorption [24]. The adsorption isotherms also show that pH has significant effect on the adsorption of benzoic acid from dilute aqueous solution is quite high at low and intermediate pH compared to the amount adsorbed at high pH. High adsorption of benzoic acid at low and intermediate pH ranges may be due to the fact that at these pH ranges benzoic acid may not be dissociated or partially dissociated into negatively charged benzoate ion and may be present predominantly as neutral benzoic acid as mentioned before. As the

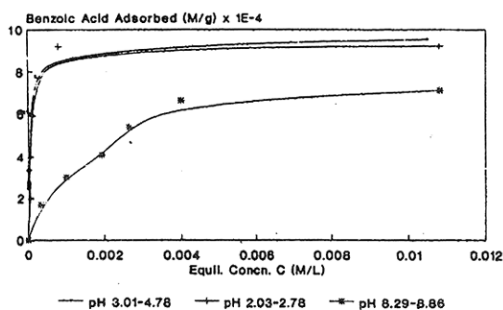


Fig. 3: Adsorption isotherms of benzoic acid on activated carbon (300 °C evaluated) at different pH.

carbon surface is mostly composed of non-polar basal plan area, these neutral species might have adsorbed to greater extent on carbon surface. At high pH benzoic acid is dissociated into negatively charged benzoate species as reported by Gould [21], and the carbon surface acquire negative charge due to adsorption of hydroxyl ion, thus due to repulsion between the negatively charged carbon surface and benzoate anion, adsorption occurs to a lesser extent at high pH compared to that low and intermediate pH. Another reason of low adsorption at high pH may be due to dissociation of oxygen functional group i.e. $-\text{COO}^-$ and $-\text{O}^-$ species, which impart negative charge to the carbon surface as has been discussed in case of benzoic acid. Thus adsorption occurs to lesser extent at high pH due to repulsion between negatively charged benzoate anion and negatively charged surface. The carbon surface after evacuation at 300 °C still retain appreciable amount of acid function group.

The adsorption isotherms of benzoic acid on activated carbon sample evacuated at 800 °C are given in Fig. 4. The concentration range varied from 4×10^{-3} to 4×10^{-2} M and pH ranges were 2.07-2.82, 3.01-6.73 and 8.38-9.02. The figure shows that the amount of benzoic acid adsorbed was quite high (approximately 3 fold) at all three pH ranges compared to the extracted and 300 °C evacuated sample under similar set of experimental conditions. This may also be attributed to the large surface of 800 °C evacuated sample compared to extract and 300 °C evacuated sample in addition to effect of surface complexes. The adsorption isotherms of benzoic acid at the three different ranges also show that pH has significant effect on the adsorption of benzoic acid. Benzoic acid was found to adsorb to

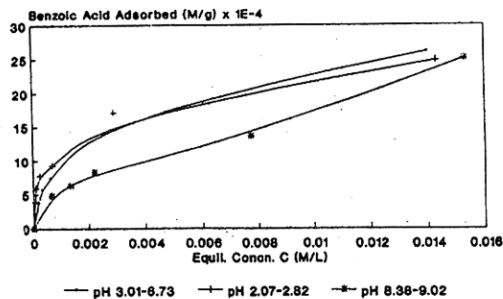


Fig. 4: Adsorption isotherms of benzoic acid on activated carbon (800 °C evaluated) at different pH.

greater extent at low and intermediate pH ranges, which may be due to the fact that benzoic acid as described earlier may not a dissociated or partially dissociated at these pH ranges into negatively charged benzoate anion and may be present predominantly as neutral benzoic acid species. As has already been discussed that the carbon surface become very non-polar after evacuation at 300 °C, which has high affinity for non-polar neutral benzoic acid species compared to high pH range, which results in greater adsorption at these pH. At high pH benzoic acid is dissociated into benzoate anion, whereas the carbon surface is very non-polar (hydrophobic), adsorption of the polar ionic species which are predominant at high pH are quite low compared to low and intermediate pH ranges.

The linear form of Freundlich's equation was applied to the isotherms data of Figures 2-4 and is depicted in Figs 5-7 in the form [26]:

$$X/m = k C^{1/n}$$

The linear form of the equation as follows:

$$\ln X/m = \ln k + 1/n \ln C$$

Where,

X/m = Amount adsorbed per gram ($\mu\text{mol/g}$)

C = Equilibrium concentration ($\mu\text{mol/L}$)

n = constant, determined from slope

k = constant, determined from intercept

The figures show that all the adsorption isotherms obey Freundlich's equation at all the three pH

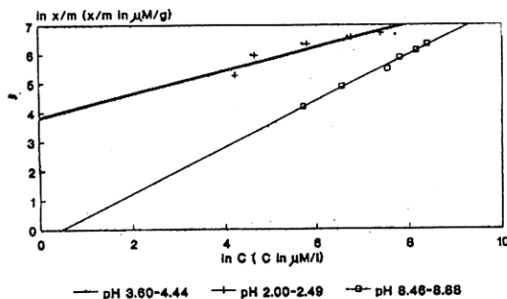


Fig. 5: Freundlich's isotherms of benzoic acid on activated carbon (extracted sample) at different pH.

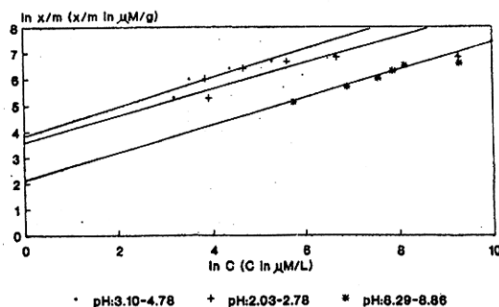


Fig. 6: Freundlich's isotherms of benzoic acid on activated carbon (300 °C evaluated) at different pH.

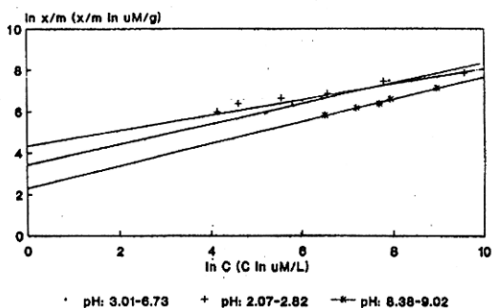


Fig. 7: Freundlich's isotherms of benzoic acid on activated carbon (800 °C evaluated) at different pH.

ranges. The adsorption capacities k of the extracted sample are 44.26, 36.60 and 1.23 $\mu\text{mol/g}$ at pH ranges 3.60-4.44, 2.00-2.49 and 8.40-8.88 respectively, showing higher adsorption capacity at 3.60-4.44 and 2.00-2.49 and lower adsorption capacity at 8.40-8.88.

The values of n are 1.54, 1.95 and 0.81 at the pH ranges 3.60-4.44, 2.00-2.49 and 8.40-8.88 respectively, showing steep slope at high pH range, indicating greater adsorption from high concentrated solution and very low adsorption from dilute solutions. This increase in adsorption with increase in concentration is relatively high at high pH compared to other two pH ranges.

The adsorption capacities k of the 300 °C evacuated sample are 46.99, 40.13 and 9.31 $\mu\text{M/g}$ at pH ranges 3.10-4.78, 2.03-2.78 and 8.29-8.86 respectively, showing high adsorption capacity at low and intermediate pH ranges and low adsorption capacity at high pH. From the values of k of extracted and evacuated sample it can easily be noticed that the adsorption capacity k for benzoic acid of the 300 °C evacuated sample are high compared to extracted sample at all the three pH ranges, which may be attributed to the high surface area of 300 °C evacuated sample compared to extracted sample. The values of n are 2.62, 2.64 and 1.67 at pH ranges 3.10-4.78, 2.03-2.78 and 8.29-8.86 respectively, showing that increase in adsorption with increase in concentration is moderate at low and intermediate pH and high at pH.

The adsorption capacities k of the 800 °C evacuated sample are 51.94, 60.34 and 9.97 $\mu\text{M/g}$ at pH ranges 3.01-6.73, 2.07-2.82 and 8.38-9.02 respectively, showing high adsorption capacity at low and intermediate pH ranges and low adsorption capacity at high pH range. Looking through the values of k of the three samples it can easily be noticed that the adsorption capacity of sample evacuated at 800 °C is high compared to other two samples. This may be due to the comparatively large surface area and mostly non-polar surface of the 800

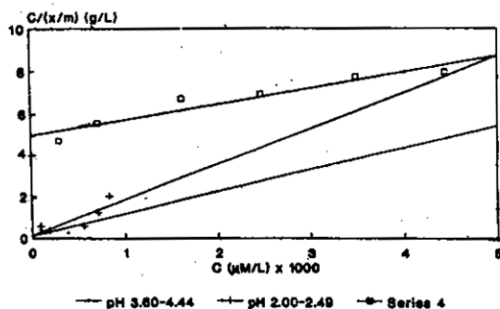


Fig. 8: Langmuir's isotherms of benzoic acid on activated carbon (extracted samples).

°C evacuated sample compared to 300 °C evacuated and extracted sample. The values of n are 1.83, 2.83 and 1.86 at pH ranges 3.01-6.73, 2.07-2.82 and 8.38-9.02 respectively indicating the increase in adsorption with increase in concentration is higher at high and intermediate pH range and moderate at lowest pH range.

The Langmuir's equation was applied to the experimental isotherms data of Figures 2-4 and has been plotted in Figures 8-10 in the following linear form [26]:

$$C/X/m = 1/ab + C/b$$

Where,

C = Equilibrium concentration ($\mu\text{mol/L}$)

X/m = Amount of solute adsorbed per gram ($\mu\text{mol/g}$)

B = Adsorption maxima

a = Binding energy constant

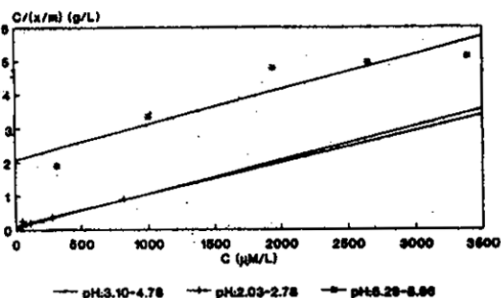


Fig. 9: Langmuir's isotherms of benzoic acid on activated carbon (300 °C evaluated) at different pH.

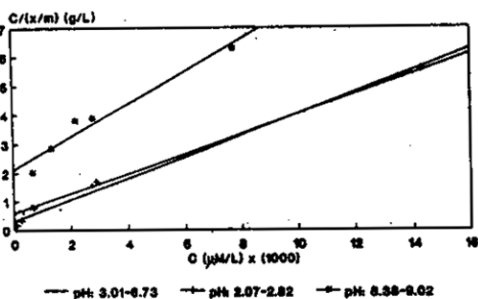


Fig. 10: Langmuir's isotherms of benzoic acid on activated carbon (800 °C evaluated) at different pH.

The figures show that all the adsorption isotherms obey Langmuir's equation as well as all the three pH ranges. The monolayer adsorption capacity b of the extracted sample are 923.57, 1043.90 and 246.86 $\mu\text{M/g}$ at pH ranges 3.60-4.44, 2.00-2.49 and 8.40-8.88 respectively, showing high adsorption at low and medium pH ranges. The monolayer adsorption capacity b of the 300 °C evacuated sample are 1042.58, 1220.61 and 764.42 $\mu\text{M/g}$ at pH ranges 3.10-4.78, 2.03-2.78 and 8.29-8.86 respectively, showing high monolayer adsorption capacity at low and medium pH ranges and low at high pH range. From the values of b , it can easily be observed that the monolayer adsorption capacity b of the 300 °C evacuated sample are high at all the three pH ranges compared to extracted sample, which may be attributed to the high surface area of the 300 °C evacuated sample compared to extracted sample, which would result in greater adsorption of benzoic acid at these pH ranges.

The monolayer adsorption capacity b of the 800 °C evacuated sample are 2376.34, 1833.67 and 1139.37 $\mu\text{M/g}$ at pH ranges 3.01-6.73, 2.07-2.82 and 8.38-9.02 showing quite high monolayer adsorption capacity at low and medium pH ranges compared to high pH. Looking through the values of b of the samples, it can easily be observed that the sample evacuated at 800 °C have high value of b at the all three pH ranges compared to other samples. Reasons for high adsorption of benzoic acid by carbon sample evacuated at 800 °C have already been discussed.

Experimental

Carbon pretreatment and degassing

Granular activated carbon 20-40 mesh Darco 7440-44-0 general brand carbon from coal raw materials obtained from Aldrich chemicals was used in the present investigation. The carbon was extracted with cyclohexane in a Soxhlet apparatus for 24 hours to remove any organic soluble substances. The extracted carbon was dried first in an ordinary oven and then a vacuum oven at $105 \pm 1^\circ\text{C}$ for 24 hours. Some of the extracted samples were also degassed under vacuum at 300°C and 800°C for 24 hours in a silica tube placed in a tube furnace. Surface area was determined by the BET method and is $979 \text{ m}^2\text{g}^{-1}$ and $1412 \text{ m}^2\text{g}^{-1}$ for the carbon samples degassed at 300 °C and 800 °C respectively. Surface acidity of carbon was determined by titration with NaOH solutions and is 345, 177 and 64 $\mu\text{equiv. g}^{-1}$ for 105, 300 and 800 °C degassed sample respectively.

Equilibrium Time

0.5 g portions of activated carbon were taken in each Erlenmeyer flasks. Fifty cm^3 of benzoic acid solution were added to these flasks having concentration of 0.0006 and 0.0012M. The content of the flasks were stirred for different duration of time at 25 °C using water bath placed on magnetic stirrer. The pH was noted before and after stirring with a pH meter. The slurries were then filtered through ordinary filter paper, discarding the first 5 cm^3 portion of the filtrate. The clear filtrate was then analyzed for benzoic acid at wavelength 269.4 nm using Shimadzu UV-160A⁰, Spectrophotometer. Blank determinations were performed under similar experimental conditions. The amount of benzoic acid adsorbed was then calculated from the difference in concentration of blank and sample. Each determination was performed in triplicate.

Adsorption Isotherms

Fifty cm^3 portions of benzoic acid solutions of different concentration ranges at various pH were introduced separately into Erlenmeyer flasks containing 0.5 g portion of activated carbon and were stirred for 4 hours at 25°C. The slurries were then filtered through ordinary filter paper. The clear filtrate was then analyzed for benzoic acid as described above.

Conclusions

It was concluded from this study that adsorption conditions like pH, surface functionalities, surface areas and porosity affect the adsorption of benzoic acid. Adsorption was maximum at intermediate pH range. Change in adsorption with pH was thought to be due to ionization of benzoic acid into cationic and anionic species and to the respective positive and negative charged surfaces of carbon, which it acquired at low and high pH. Further, adsorption was increased with degassing of carbon at high temperature. This might be due to the comparatively non-polar surface and large surface area of the carbon samples degassed at high temperatures. Freundlich and Langmuir's equations were applied to the isotherms data of benzoic acid and both were found to be obeyed well.

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