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# EFFECT OF DIFFERENT PARAMETERS ON THE ADSORPTION OF TOXIC ALIPHATIC AMINES ON CHARCOAL

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Commercial granular charcoal was degassed at 105°C, 300 °C and 800 °C for a period of twenty four hours, which was then used as an adsorbent for the adsorption of methylamine, dimethylamine and trimethylamine from their aqueous solutions at 25°C. The time dependence studies showed four hours optimum time for the maximum adsorption of the alkyl amines, irrespective of their nature and concentration (0.005M, 0.01M). Adsorption was greater from higher concentration than lower concentration of adsorbate solution. Lower adsorption of alkylamines was observed when the charcoal was evacuated at high temperature. The adsorption sequence of alkylamines followed the order dimethylamine > trimethylamine > methylamine.

**Keywords**: Adsorption, Aliphatic amines, Charcoal, Toxicity, Purification

## 1. Introduction

The organic compounds have many applications in chemical and food industries but have got many toxic effects as well [1]. The extensive use of organic compounds in industries like textile, agriculture, tanning and dairy are of growing concern now a days for environmentalists, due to their toxicity to aquatic as well as human lives, upon entering into aqueous streams through discharge of these industrial and municipal wastes [2]. Such type of polluted water needs to be treated before human consumption. Various techniques have been used by earlier investigators for the removal of pollutants but the adsorption technique due to its high pollutant uptake capacity, effective treatment in dilute solutions, low cost and regeneration ability is considered a popular approach [3].

Granular activated charcoal (GAC) is a potential adsorbent for the removal of both synthetic as well as naturally occurring organic material from water and wastewater. Granular charcoal is a microporous-type adsorbent and can be made from a variety of carbonaceous materials, mainly biological in origin through process of carbonization followed by activation process [4]. The alkyl amines are toxic to human by means of body contact. They cause destructive skin burning and when swallowed lead to serious corrosive injury. Particularly methylamine is irritant to eyes, skin and respiratory tract [5]. The adsorption of organic compounds on surface of modified activated carbon was studied earlier [6]. Karanfil and Kilduf [7] demonstrated the role of granular activated carbon surface chemistry on the adsorption of trichloroethylene and trichlorobenzene. Other parameters such as pore size [8], surface physico-chemical characteristics of activated carbon [9] and activity of different activated carbons [10] influence the adsorption on its surface.

The present study is focused to investigate the equilibrium time, concentration, influence of functional groups and the ability of toxic aliphatic compounds using commercial granular activated charcoal as an adsorbent. This study will help in exploring the use of GAC as a potential material from environmental point of view to remove the toxic materials by adsorption.

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## 2. Materials and Methods

In the present investigation commercial charcoal was selected for adsorption studies as an adsorbent. The charcoal was pretreated to increase its adsorptive properties. The activation of charcoal sample was carried out by chemical and thermal activation process. Granular commercial charcoal was mixed with 0.1N $HNO_3$ and 0.1 HCl solutions in a ratio of 1:1. The slurry was stirred manually for 24 hours, filtered through Wattman filter paper (# 3), washed repeatedly with doubled distilled water and dried in electric oven at 105 $^oC$. The resultant sample was cooled in desicator and stored in the airtight storage bottles. Organic compounds were removed using sohxlet extractor. The extracted sample was dried in a vacuum oven at 105 $^oC$ for 24 hours. The sample was cooled under vacuum and stored in airtight bottles. The evacuation was carried out in tube furnace by taking the dried sample in silica tube, connected to ½ horse power vacuum pump to remove the volatile contents. The sample was evacuated at elevated temperatures of 200 $^oC$, 300 $^oC$, 400 $^oC$, 600 $^oC$, 800 $^oC$ and 1000 $^oC$ for 24 hours. The resultant sample was gradually cooled in and stored in airtight bottle under inert atmosphere of nitrogen. Vacuum oven, model precision 919 USA and tube furnace, model 215 Gallenkamp, England were used. All the reagents used were of analytical grade and all solutions were made in double distilled water.

One litre of stock solution of adsorbate (0.1M) was prepared by diluting appropriate volume of methylamine, dimethylamine and trimethylamine respectively. Stock solution of 0.1M HCl was prepared and standardized by titrating against standard 0.1M NaOH solution. Each adsorbate solution was standardized by titrating against standard 0.1M HCl using mixed indicator. For adsorption studies the working solutions of 0.002, 0.004, 0.006………. 0.018M strength were prepared by dilution method. Bromocresol green (0.1%) indicator was prepared by dissolving 0.1g of bromocresol green powder in 100ml of methanol. Methyl red (0.1%) indicator was prepared and used. Mixed indicator was prepared by mixing five parts of 0.1% solution of bromocresol green and one part of 0.1% of methyl red solution. Adsorption equilibrium was studied using following experimental conditions:

Adsorbate volume: 50 ml

Adsorbate concentration: 0.005M and 0.01M

Adsorbent dose: 0.5 g

Stirring temperature: 25 $^oC$

Stirring time: ½, 1, 2, 4, 6 and 8 hours

Granular activated charcoal (0.5g) was taken in 3 flasks. To each flask 50 ml of adsorbate were added, closed by stopper, stirred for various duration of times at 25 $^oC$ and filtered. A known volume of filtrate was titrated against 0.005M HCl using mixed indicator. The colour of mixed indicator changes from bluish red to reddish orange. The amount of adsorbed amines were calculated by the following relationship.

$$W = \frac{(C_i - C_f) \times V}{S \times 1000}$$

where,

W is the amount of adsorbate adsorbed (mol/g),

$C_i$ is the initial concentration of adsorbate (mol/L),

$C_f$ is the equilibrium concentration of adsorbate (mol/L),

V is the Volume of adsorbate (ml),

and S is the amount of adsorbent (g)

The optimum uptake was observed after 4 hour and for the subsequent adsorption studies 4 hour was used as a stirring time. Adsorption measurement of alkyl amines at constant temperature (25 $^oC$) was carried out by batch technique. A known quantity (0.5g) of adsorbent evacuated at 105 $^oC$, 300 $^oC$ and 800 $^oC$ was stirred for 4 hour. The slurry was filtered and the unabsorbed amine was determined by volumetrically. The equilibrium concentration of adsorbate was calculated by titrating against HCl (0.005M and 0.01M) solutions. The effect of evacuation temperature on adsorption of aliphatic amines was studied by taking 0.5g evacuated samples at different temperatures (200 $^oC$, 400 $^oC$, 600 $^oC$, 800 $^oC$ and 1000 $^oC$). To each flask 50 ml of adsorbate were added, stirred for 4 hour under thermostatically controlled temperature (25 $^oC$) and filtered. A known volume of filtrate was titrated against standard HCl solution to know the equilibrium concentration of adsorbate. Statistical analysis of the data was conducted by standard method [11].

## 3. Results and Discussion

### *3.1. Effect of equilibrium time*

The adsorption of alkylamines on GAC at 25 $^{o}$C, as a function of contact time (0.5, 1, 2, 4, 6 and 8 hrs) was conducted. The effect of concentration and nature of adsorbate molecules on the optimum time were also studied. The variation in adsorption with contact time can be viewed from Tables 1-3. The data show that the adsorption in the early stages increases more rapidly with increase of contact time and reach the maxima and become almost constant at four hours, referred to as equilibrium time. This shows that in the early stages of adsorption a large number of active sites are available on the surface of granular activated charcoal. Initially, the surface to alkylamines interaction is more. As adsorption proceeds, the

Table 1. Adsorption of methylamine on GAC at different stirring time.

| Stirring time (hrs) | Equilibrium concentration (mol/L) | Amount adsorbed (mol/g) | Equilibrium concentration (mol/L) | Amount adsorbed (mol/g) |
|---|---|---|---|---|
| | 0.005M | | 0.01M | |
| 0.5 | 0.00348 | 0.00015 | 0.00790 | 0.00021 |
| 1.0 | 0.00308 | 0.00019 | 0.00730 | 0.00027 |
| 2.0 | 0.00296 | 0.00020 | 0.00680 | 0.00032 |
| 4.0 | 0.00290 | 0.00021 | 0.00660 | 0.00034 |
| 6.0 | 0.00290 | 0.00021 | 0.006580 | 0.00034 |
| 8.0 | 0.00290 | 0.00021 | 0.00660 | 0.00034 |

Table 2. Adsorption of dimethylamine on GAC at different stirring time.

| Stirring time (hrs) | Equilibrium concentration (mol/L) | Amount adsorbed (mol/g) | Equilibrium concentration (mol/L) | Amount adsorbed (mol/g) |
|---|---|---|---|---|
| | 0.005M | | 0.01M | |
| 0.5 | 0.00360 | 0.00014 | 0.00770 | 0.00023 |
| 1.0 | 0.00304 | 0.00020 | 0.00677 | 0.00032 |
| 2.0 | 0.00274 | 0.00023 | 0.00060 | 0.00040 |
| 4.0 | 0.00260 | 0.00024 | 0.00570 | 0.00043 |
| 6.0 | 0.00260 | 0.00024 | 0.00570 | 0.00043 |
| 8.0 | 0.00260 | 0.00024 | 0.00570 | 0.00043 |

Table 3. Adsorption of trimethylamine on GAC at different stirring time.

| Stirring time (hrs) | Equilibrium concentration (mol/L) | Amount adsorbed (mol/g) | Equilibrium concentration (mol/L) | Amount adsorbed (mol/g) |
|---|---|---|---|---|
| | 0.005M | | 0.01M | |
| 0.5 | 0.00340 | 0.00016 | 0.00780 | 0.00022 |
| 1.0 | 0.00300 | 0.00020 | 0.007140 | 0.00029 |
| 2.0 | 0.00286 | 0.00021 | 0.00670 | 0.00033 |
| 4.0 | 0.00280 | 0.00022 | 0.00640 | 0.00036 |
| 6.0 | 0.00280 | 0.00022 | 0.00640 | 0.00036 |
| 8.0 | 0.00280 | 0.00022 | 0.00640 | 0.00036 |

active sites of surface become saturated and there is no more adsorption, with the increase of contact time. The concentration of adsorbates has no effect on the equilibrium time. Tables 1-3 also show the effect of nature of adsorbate molecules on the equilibrium time. Furthermore, the selectivity of alkylamines can be easily visualized from the extent of adsorption. The selectivity sequence observed, lies in the order as dimethylamine > trimethylamine > methylamine. The degree of uptake of these amines by GAC may be depending on the solubility and basicity of amines in water. According to the literature [12] substances of lower solubility are adsorbed easily on the surfaces. In our studies the solubility of monomethylamine is higher than that of dimethylamine and trimethylamine. Further, dimethylamine shows higher basicity, while trimethylamine is more basic than methylamine. Thus both the solubility and basicity of alkylamines play a pivtol role in the selectivity of adsorbate towards activated charcoal i.e. less soluble and more basic amines were more adsorbable than that of higher soluble and low basic alkylamines. The findings of present study were in good agreement with the reported results [5,13].

*3.2. Adsorption study at constant temperature*

Adsorption of alkylamines on GAC, evacuated at 105$^0$C, 300$^0$C and 800 $^o$C was performed at constant temperature (25 $^o$C) and the results are shown in Figures 1-3. These figures show that the adsorption increases with an increase of equilibrium concentration and attain a plateau at higher equilibrium concentration. This may be due to the presence of active sites on the GAC surface. At lower concentration of adsorbate, there is abrupt rise of the isotherms as seen in the Figures 1-3. At higher concentration, the isotherm increases slowly and finally the isotherm becomes linear due to the surface saturation. Similar behavior has been observed earlier [14]. The charcoal evacuated at 105$^0$C has much prominent adsorption capacity, than the samples evacuated at 300$^0$C and 800$^0$C, this uptake capacity order follows the trend as 105$^0$C>300$^0$C>800$^0$C. This adsorption trend may be due to the interaction of adsorbate with surface acidic sites. It is reported that the charcoal surface is composed of acidic groups such as lactones, phenolic, hydroxyl, carboxylic, quinone, carboxylic acid, anhydride and cyclic peroxide [15]. At low evacuation temperature (105 $^o$C) the surface groups are still present with the exception of moisture removal, which may interact with the alkylamines and thus have greater adsorption

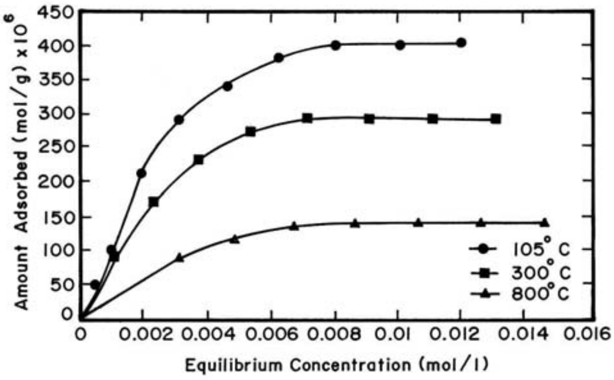


Figure 1. Uptake of methylamine on GAC evacuated at different temperatures.

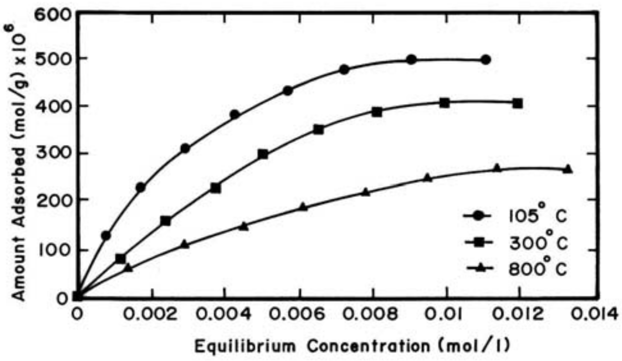


Figure 2. Uptake of dimethylamine on GAC evacuated at different temperatures.

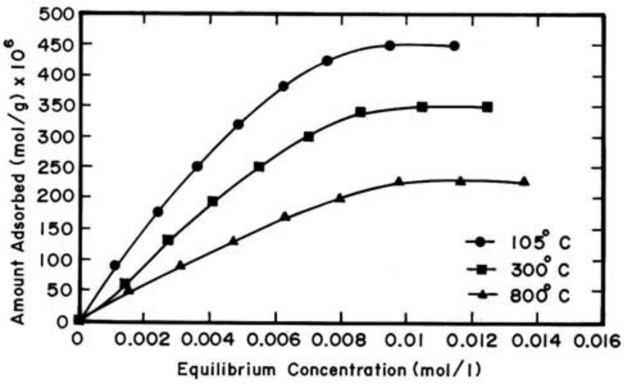


Figure 3. Uptake of trimethylamine on GAC evacuated at different temperatures.

while in the high temperature treatment, the surface functional groups may decompose with the evolution of CO and $CO_2$ resulting in lower adsorption of amines [16]. It may be concluded that at low temperature a large number of acidic sites are present at the surface, the extent of amines adsorption is more. At high temperature evacuation the magnitude of acidic sites decreases and the absorption of amines on higher evacuated temperature sample decreases. These observations reveal that the adsorption of amine follows through complexation or interaction with

Table 4. Effect of evacuation temperature on adsorption of methylamine.

| Temp ($^0$C) | Initial concentration (0.004M) | | Initial concentration (0.016M) | |
|---|---|---|---|---|
| | Equilibrium concentration (mol/L) | Quantity adsorbed (mol/g) | Equilibrium concentration (mol/L) | Quantity adsorbed (mol/g) |
| 200 | 0.00240 | 0.00016 | 0.01210 | 0.00039 |
| 400 | 0.00280 | 0.00012 | 0.01320 | 0.00028 |
| 600 | 0.00310 | 0.00009 | 0.01410 | 0.00019 |
| 800 | 0.00336 | 0.00006 | 0.01460 | 0.00014 |
| 1000 | 0.00340 | 0.00006 | 0.01464 | 0.00014 |

Table 5. Effect of evacuation temperature on adsorption of dimethylamine.

| Temp ($^0$C) | Initial concentration (0.004M) | | Initial concentration (0.016M) | |
|---|---|---|---|---|
| | Equilibrium concentration (mol/L) | Quantity adsorbed (mol/g) | Equilibrium concentration (mol/L) | Quantity adsorbed (mol/g) |
| 200 | 0.00230 | 0.00017 | 0.01190 | 0.00041 |
| 400 | 0.00290 | 0.00011 | 0.01250 | 0.00035 |
| 600 | 0.00320 | 0.00008 | 0.01300 | 0.00030 |
| 800 | 0.00340 | 0.00006 | 0.01330 | 0.00027 |
| 1000 | 0.00344 | 0.00006 | 0.01340 | 0.00026 |

Table 6. Effect of evacuation temperature on adsorption of methylamine.

| Temp ($^0$C) | Initial concentration (0.004M) | | Initial concentration (0.016M) | |
|---|---|---|---|---|
| | Equilibrium concentration (mol/L) | Quantity adsorbed (mol/g) | Equilibrium concentration (mol/L) | Quantity adsorbed (mol/g) |
| 200 | 0.00210 | 0.00019 | 0.01150 | 0.00045 |
| 400 | 0.00260 | 0.00014 | 0.01240 | 0.00036 |
| 600 | 0.00280 | 0.00012 | 0.01310 | 0.00029 |
| 800 | 0.00300 | 0.00010 | 0.01350 | 0.00025 |
| 1000 | 0.00310 | 0.00009 | 0.01370 | 0.00023 |

surface acidic groups and little effect of micropores created with activation is observed. The uptake increases from monomethylamine to dimethylamine, whereas from dimethylamine to trimethylamine the extent of uptake decreases in the concentration range studied. It may be due to the lower solubility of dimethylamine in water. As reported in the literature [5], the lower soluble adsorbate has greater adsorption capacity.

### *3.3. Effect of evacuation temperature on the uptake of alkylamines*

The effect of GAC evacuated at 200 $^o$C, 400 $^o$C, 600 $^o$C, 800 $^o$C and 1000 $^o$C on the adsorption of alkylamines is presented in Tables 4-6. The data indicated that the alkylamines adsorption decrease with an increase in the evacuation temperature. Initially the evacuation temperature increment has a much more prominent effect on the uptake of alkylamines i.e. the extent of adsorption decrease sharply till reaches to 800 $^o$C. However, further evacuation of GAC has no significant effect on the extent of adsorption of amines and the amount of adsorption becomes almost constant above this temperature. Therefore, the surface to amine interaction, seem to be due to the acidic sites on the surface of activated charcoal, thus binding sites for the alkylamines molecules decreases which ultimately reduces the extent of adsorption. Further, the decrease in the extent of adsorption with evacuation of GAC follows same behaviour for all adsorbates studied. However, the only observable change is the high uptake of amines by GAC at concentration of 0.016M than 0.004M concentration of adsorbate.

## 4. Conclusions

It is observed that both the solubility and basicity of alkylamines play a crucial role in selecting the best adsorbate towards activated charcoal i.e. less soluble and more basic amines will more effectively be removed from aqueous medium than that of higher soluble and lower basic alkylamines. It is concluded that at low temperature treatment a large number of surface acidic sites are present at surface consequently, the extent of amines adsorption is more while at high temperature, the surface acidic sites decreases and hence, the adsorption of amines decreases. It is also observed that the alkylamines adsorption decrease with the increase in evacuation temperature, till reaches to 800 $^{o}$C, and the amount of adsorption becomes almost constant above this temperature. Overall, the extent of adsorption was highest for dimethylamine, followed by trimethylamine and lowest for methylamine.

## References

[1] R.A. Dobbs and J.M. Cohen, Carbon adsorption for toxic organic, EPA 600/8-80-023, Municipal Environ.Lab., Cincinnati, Ohio, USA, 45268, April (1980).

[2] R.W. Walter and R.G. Luthy, Environ. Sci. Technol., **18** (1984) 395.

[3] D. Mohammad and R. Hussain, Sci. Int. Lhr, Pak., **4** (1992) 143.

[4] G. Foly, Charcoal making in developing countries, Tech. Report No. 5. 11th Edn. London (1986).

[5] D.S. Foster, Encyclopedia of Industrial Chemical Analysis, Vol. 5, Inter Sci. Pub. New York (1967).

[6] Uranowski and J. Lais, Water Res., **23** (1998) 1841.

[7] K. Tanju and E.K. James, Environ. Sci. Technol. **33** (1999) 3217.

[8] N.A. Eltekova and Y.A. Eltekova, Carbon **31** (1993) 957.

[9] Y.C. Chiang P.C. Chiang and E.E. Chang, Environ. Sci. Health **33** (1998) 1437.

[10] T.M. Lupashku, Larisa, Rev. Roum. Chim. **39** (1994) 909.

[11] M. Little and F.J. Hills, Agric. Extension, Univ. California,Davis, USA, (1972).

[12] D.O. Cooney, Water Res. **1** (1983) 7403.

[13] G.C. Walter and A.R. Robert, Can. J. Chem. **51** (1973) 533.

[14] I. Yousaf, A. Sultan and I. Mohammad, J. Chem. Soc. Pak. **22** (2000) 281.

[15] J.K. Thompson, J.J. Krebs, H.A. Resing, Chem. Phys. **43** (1965) 3853.

[16] J.W. Hasseler, Activated Carbon, Chemical Pub. Co., New York (1974).