
Influence of Parameters on Adsorption of Aromatic Compounds From N-paraffins using Commercial Adsorbents

Anil Yadav

Department of Chemical Engineering,
DeenbandhuChhotu Ram University of Science & Technology,
Murthal, Sonapat, Haryana, India

ABSTRACT

The main aim of this research was to study the influence of different parameters and separate the aromatic compounds, benzene, toluene; and n-hexane from aqueous solutions by adsorption on commercial activated carbons, sodium exchanged zeolite X and activated alumina. The affecting parameters studied were adsorbent dosage, pH and temperature. The experiments were conducted in batch adsorbents. The adsorption of benzene, toluene and n-hexane on activated carbon, sodium exchanged Zeolite X and activated alumina 13X molecular sieves have been studied in liquid phase at temperatures 30, 50 and 60°C and 1 atm pressure. The adsorption data was fitted into Langmuir and Freundlich isotherms. It was observed that Langmuir equation fits the experimental isotherm data better than the Freundlich equation. The saturation adsorption capacities of adsorbates were determined.

The kinetic experimental data was fitted into the Lagergren's pseudo-first order and pseudo second-order systems. It was observed that pseudo second-order kinetic model fits experimental data very well. The kinetic rate constants and amount of adsorption capacities were reported for different adsorbents. The maximum uptake capacity for benzene at 30°C using 13X molecular sieve was calculated. Benzene was more selective for adsorption towards 13X molecular sieves than other adsorbents.

Keywords: adsorption, activated carbon, Zeolite, selectivity, adsorption capacity

1. Introduction

Different technologies such as biodegradation, solvent extraction, chemical precipitation, membrane separation, ion exchange and many others have been employed to treat contaminants. Adsorption is frequently used to remove pollutants in wastewater because the application of other techniques entails high costs. Among all these separation technologies adsorption is the efficient method of separation. Activated carbon adsorption is an important separation technology, which is widely used in Chemical and Environmental engineering.

Activated carbon has a variety of surface groups, impurities and irregularities with the pore sizes ranging from micropores to macropores that are randomly connected in their pore networks [12]. Activated carbons have been widely employed as adsorbents in decontamination processes due to their high adsorption capacity, fast adsorption kinetics, ease of regeneration, extended surface area, microporous structure and special surface reactivity [9]. Many types of carbonized raw materials can be activated by means of steam activation or chemical activation [13]. The adsorption capacity of activated carbons, Zeolite depend on various factors such as surface area, pore distribution and surface functional groups of activated carbon, polarity, solubility, pH and concentration of adsorbate and so on [9-10].

Apart from these other adsorbents like ZeoliteNaX, molecular sieve and activated alumina can also be used because of their increased adsorption capacity to improve separation of aromatic compounds from n-paraffins.

Many studies have been reported on the adsorption of organic compounds from gas stream. Limited studies were reported on the adsorption from aqueous solution. The liquid phase adsorption is a more complicated process than gas or vapor phase adsorption [11]. Therefore, the main aims of this research were to study the influence of different parameters and adsorption of benzene, toluene and n-hexane from n-paraffin on activated carbons, Zeolite NaX molecular sieve and activated alumina for better understanding of kinetics and thermodynamic of the adsorption process.

2. Experimental details

Solution preparation

The solution was prepared from mixing the benzene and n-hexane. The 0.1g of benzene was added with 9.9g of the n-hexane to prepare 1 wt% sample which is equal to the 10000ppm or 10000mg/l. further dilutions were made from the 1 wt% solution with the help of hexane as solvent.

The 3ml solution from 10000ppm is further diluted with 27ml of n-hexane to make a solution of 30ml of 0.1wt% or 1000ppm. Similarly further dilutions were made from the 1000ppm solution. The 3ml solution from the 1000ppm is further diluted with 27ml of n-hexane to make a solution of 0.01 wt % or 100ppm. The dilutions like 10, 20, 40, 60 ppm were made from the 100ppm solution in similar manner.

Zeolite Molecular Sieves

Zeolite molecular sieve have been used in this work for the removal of benzene from n-hexane in solution. Zeolite 13X is in the form of cylindrical beads with 1.5 mm diameter. Zeolite beads used in this work have 70% clay and 30% binder. Other adsorbents used in the study were activated carbon and activated alumina.

Chemicals and reagents

Experimental chemicals were of AR and LR grades. Double distilled water was used for all experiments. The mixture of benzene and hexane were used for this study. The chemicals used for experimentation was Benzene, n-Hexane, Acetone, HCl, Sodium Acetate, and each chemical was purchased from Merck Company. Adsorbents Activated Alumina, Activated Carbon, 13X and 4A molecular sieves were procured from IPCL/ACE manufacturing & marketing, Vadodara.

Different buffers were prepared over a range of 2-7pH so as to study the effect of pH on the removal efficiency of all the adsorbents. For maximum range of pH, Solution of Acetic acid and Sodium Acetate were used for maintaining the pH of the solution. For the analysis of solution the chemicals used were hydrochloric acid, acetone, acetic acid and sodium acetate.

UV-Vis (Ultraviolet-visible) spectrophotometer (Ultra 3660) of RIGOL Company was used to check absorbance.

Methodology

Treatment of the Molecular sieve/Zeolites

The molecular sieves or zeolites were treated depends on the requirements. Before using, these were first activated at 350 °C for 2 hours to remove the moisture from molecular sieve/zeolites.

Analysis of different concentrations in aqueous solution

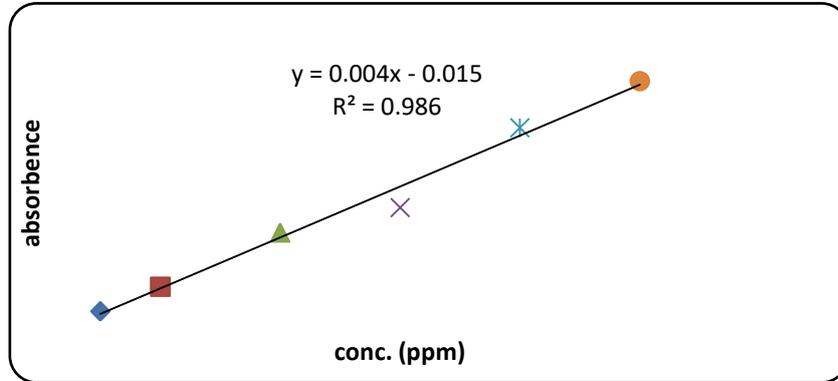
Concentrations of unknown solution were determined by UV- Vis spectrophotometer. A calibration curve had been obtained from Beer's Lamberts law. The Beer-Lambert law is written as $A = \epsilon \cdot b \cdot c$ where ϵ shows the wavelength-dependent molar absorptivity coefficient with units of $M^{-1} \text{ cm}^{-1}$.

3. Results and Discussion

Calibration Curve from Beer Lamberts law:

The following is the calibration curve obtained by plotting concentration versus absorbance.

Fig. 1: Calibration curve for the benzene-hexane system



The calibration curve obtained from the beer lambert’s law. It states that the absorbance is directly proportional to the concentration. Figure 1 shows that as the concentration of solution increases the absorbance also increased.

CONCENTRATION (ppm)	ABSORBANCE (nm)
10	0.032
20	0.074
40	0.166
60	0.208
80	0.343
100	0.422

Table 1: Variation of concentraion with adsorption from beer’s law for benzene-hexane system

Batch experiments to Study the Influence of Parameters:-

Batch experiments were carried out to study the influence of optimum temperature, adsorbent dose, contact time, pH , equilibrium isotherm and kinetics of adsorption.

A. Effect of Temperature

Different sets of experiments were conducted at different concentrations starting from 10 ppm to 60 ppm at different temperatures at 30, 40 and 50 °C.

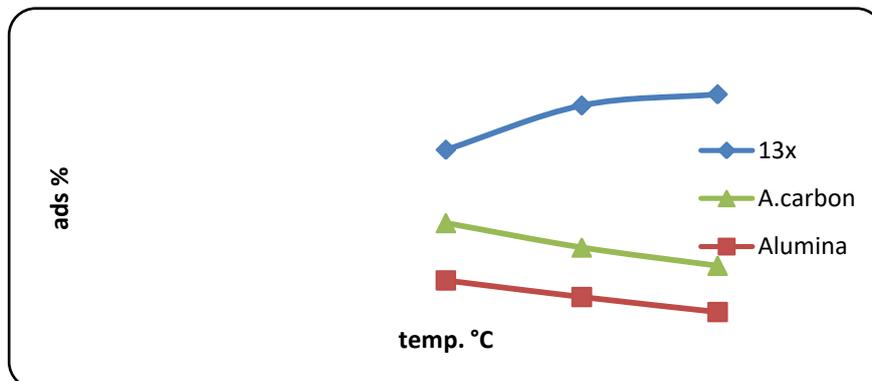


Figure 2: Variation of adsorption capacity with the temperature.

As the temperature increases the adsorption capacity of the molecular sieves gets decreased except 13X molecular sieve whose adsorption increases with increase in temperature but after a certain temperature it decreases because it reaches the boiling point of the hexane.

Temperature °C	13X Molecular Sieve	Activated Carbon	Activated Alumina
30 °C	3.256	2.117	1.224
40 °C	3.946	1.736	0.968
50 °C	4.120	1.452	0.736
60 °C	3.146	0.864	0.453

Table 2: Effect of temperature on adsorption of different adsorbents

B. Effect of the amount of adsorbent

In Experimentation it was found that maximum adsorption was achieved at adsorbent dose of 1gm.

C. Effect of pH

As the pH of the system shifts from acid to basic, the adsorption increases and after value of pH 5.5 it suddenly decreases. The optimum pH in case of molecular sieves was found to be in the range of 5.0-5.5 but in case of 13X adsorption was maximum at 5.5 pH. So the adsorption experiments were carried out at 5.5 pH.

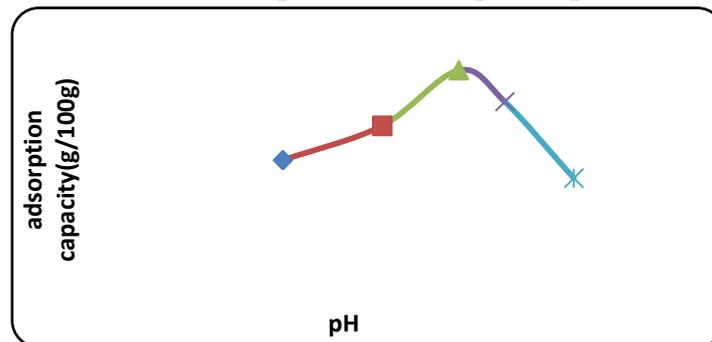


Figure 3: Effect of pH on adsorption of system for 13X

The pH plays an important role in this process. Specially in case of the molecular sieves/zeolites as the pH of system decreases the bonds present in zeolites break due to rupture of the clay or binder pores and on the other hand as the pH shifted towards the basic, the pore opening in zeolites cause problem i.e. the pores are blocked if the system is highly basic.

D. Effect of contact time

Contact time is an important factor in adsorption process. More the contact time better is adsorption.

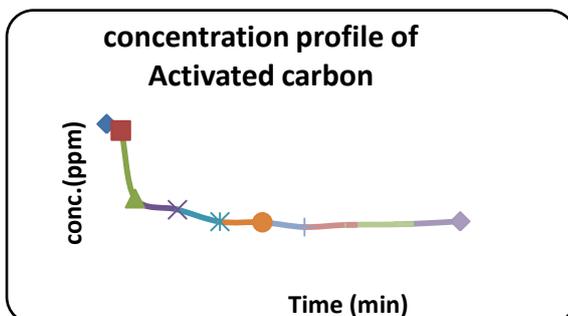


Fig 4 : Change in concentration of activated carbon at 30 °C

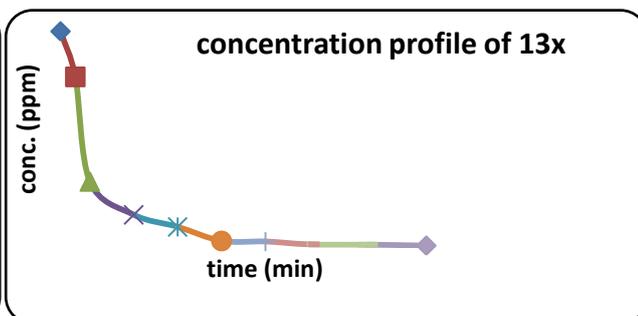


Fig 5: Change in concentration of 13X molecular sieve at 30 °C

fig.4 shows as the time proceed the bulk phase concentration get reduced due to the adsorption of the adsorbate phase molecules on to adsorbent. In case of activated carbon the equilibrium was achieved in 45 minutes. The adsorbents were contacted with adsorbate for 2 hour 10 minutes. In this time lap the complete adsorption of the system taken place which can be indicated from the concentration of the system

fig.5 shows as the time proceed the bulk phase concentration get reduced due to the adsorption of the adsorbate phase molecules on to adsorbent. In case of 13X molecular sieve the equilibrium is reached in 30 minutes. The bulk phase concentration reduced to a minimum level where adsorbent is completely saturated. The adsorbents are contacted with adsorbate for 2 hour 10 minutes. In this time lap the complete adsorption of the system taken place.

4Determination adsorption capacity of adsorbents by adsorption isotherm curves:

Adsorption isotherm experiments were performed in batch mode using benzene in n-hexane and zeolite at temperature (30°C). In order to generate adsorption isotherm curves, experiments were performed at different initial concentrations of adsorbate keeping other parameters constant.

Experimental data fitting into Langmuir equation is shown in Figures 6, 7 and 8 at temperature 30°C respectively:

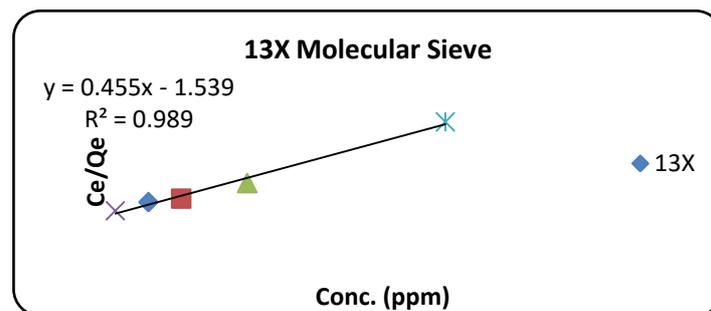


Fig. 6 : Fitting experimental data into Langmuir equation (linearized) plot of 13X molecular sieve.

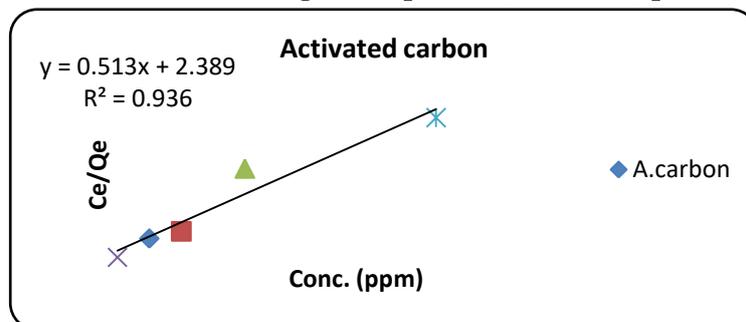


Fig.7: Fitting experimental data into Langmuir equation (linearized) plot of Activated Carbon.

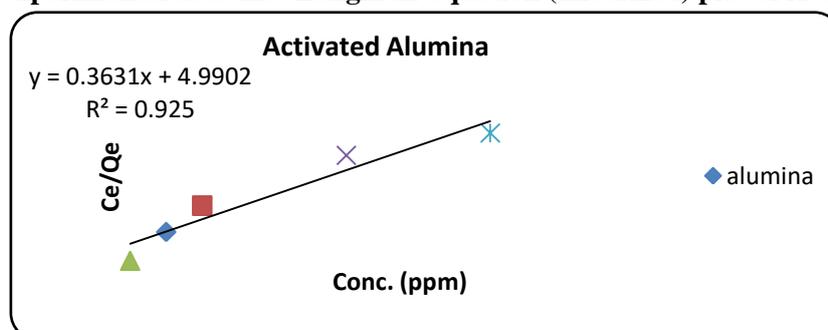


Fig.8 : Fitting experimental data into Langmuir equation (linearized) plot of Activated Alumina.

Adsorbent	q_m	k
Activated Alumina	3.165	0.037
Activated carbon	2.033	0.127
13x Molecular Sieve	2.137	0.188

Table 3: Values of q_m and K using Langmuir equation

In one experimental run, about 3ml of feed solution was contacted with about 1.0g of the adsorbent for 3-4 hr at desired temperature. Then, samples before and after adsorption were analyzed, and from values of concentration quantity of benzene adsorbed was calculated.

Conclusions

Adsorption isotherms of benzene on zeolites or molecular sieves were studied in liquid phase at temperature 30 °C, 40 °C and 50 °C. The equilibrium of adsorption was described by Langmuir isotherm. The Langmuir equation fits the experimental data ($q_m = 2.137$ and $k = 0.188$ for 13X molecular sieve at 30 °C) better than the others isotherm. The **adsorption capacity** of the adsorbent is maximum at 30 °C for activated carbon ($q = 2.117$). Benzene is more selective towards 13X molecular sieve than other molecular sieves.

Adsorbent	q_m	k
Activated Alumina	3.165	0.037
Activated carbon	2.033	0.127
13x Molecular Sieve	2.137	0.188

References

- H. Hindarso, S. Ismadji, F. Wicaksana, N. Mudjijati, Indraswati, Adsorption of benzene and toluene from aqueous solution onto granular activated carbon, *J. Chem. Eng. Data* 46 (2001) 788–791
- VON BURG, R. Toxicology update: toluene. *Journal of applied toxicology*, **13**: 441–446(1993).
- Odor thresholds for chemicals with established occupational health standards. Fairfax, VA, *American Industrial Hygiene Association*, 1989.
- Toluene*. Geneva, World Health Organization, 1985 (Environmental Health Criteria, No. 52).
- Chemical and engineering news*, April 10, 1995.
- American conference of governmental industrial hygienists; Notice of intended changes – toluene, trim ethylamine, and vinyl acetate. *Applied occupational and Environmental hygiene*, 6:966–977 (1991).
- Low, L.K., Meeks, J.R. & Mackerer, C.R. Health effects of the alkylbenzenes: toluene. *Toxicology and industrial health*, **4**: 4–75 (1988).
- Tarley, C. R. T. and M. A. Z. Arruda. 2003. Biosorption of heavy metals using rice milling by-products Characterization and application for removal of metals from aqueous effluents. *Chemosphere* 54: 987-995.
- Koh, M.; Nakajima, T. Adsorption of aromatic compounds on C_xN-coated activated carbon. *Carbon* **2000**, 38, 1947-1954.
- Aksu, Z. and Yener, J. 2001. A Comparative Adsorption/biosorption Study of Mono-chlorinated Phenol onto Various Sorbents, *Waste Manag.*, 21: 695-702.
- Castilla, C. M. Adsorption of organic molecules from aqueous solutions on carbon materials. *Carbon* **2004**, 42, 83–94.
- Ismadji, S., and Bhatia S.K., “Use of Liquid Phase Adsorption for Characterizing Pore Network Connectivity in Activated Carbons” *2000 AIChE Annual Meeting*, Los Angeles, California, 12-17 November 2000.
- Jung, M. W., Ahn, K. H., Lee, Y., Kim, K. P., Rhee, J. S., Park, J. T. and Paeng, K. J. 2001. Adsorption Characteristics of Phenol and Chlorophenols on Granular Activated Carbon (GAC), *Microchem. J.*, 70: 123-131.
- Wong, Y. C.; Szeto, Y. S.; Cheung, W. H.; McKay, G. *Process Biochem.* **2004**, 39, 695.
- Slejko, F.L., 1985. *Adsorption Technology: a Step-by-Step Approach to Process Evaluation and Application*. Marcel Dekker, New York.

-
16. Koh, S-M. and Dixon, J.B., (2001). Preparation and application of organo-minerals as sorbents of phenol, benzene and toluene. *Appl. Clay Sci.*, **18**, 111-122.
 17. Lin, S.H., Huang, C.Y., Modeling of aqueous BTEX adsorption in column and multistage adsorbers, *J. Environ. Eng., ASCE* 126 (2000) 802–806.
 18. Khan, A.R., Atallah, R., Al-Hadded, A. (1997) Equilibrium adsorption studies of some aromatic pollutants from dilute aqueous solutions on activated carbon at different temperatures. *Journal of Colloid and Interface Science*, 194 (1): 154
 19. Cosultchi, A., Bosch, P. and Lara, V. H. , *Coll. Polym. Sci.* **281**, 325 (2003)
 - 20 Furuya, E.; Sato, K.; Kataoka, T.; Horiguchi, T.; Otake, Y. *Sep. Purif. Technol.* 2004, 39, 73– 78