A

Seminar report

On

Activated Carbon Adsorption

Submitted in partial fulfillment of the requirement for the award of degree Of Civil

SUBMITTED TO:

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Preface

I have made this report file on the topic **Activated Carbon Adsorption**; I have tried my best to elucidate all the relevant detail to the topic to be included in the report. While in the beginning I have tried to give a general view about this topic.

Acknowledgement

I would like to thank respected Mr...... and Mr......for giving me such a wonderful opportunity to expand my knowledge for my own branch and giving me guidelines to present a seminar report. It helped me a lot to realize of what we study for.

Secondly, I would like to thank my parents who patiently helped me as i went through my work and helped to modify and eliminate some of the irrelevant or un-necessary stuffs.

Thirdly, I would like to thank my friends who helped me to make my work more organized and well-stacked till the end.

Next, I would thank Microsoft for developing such a wonderful tool like MS Word. It helped my work a lot to remain error-free.

Last but clearly not the least, I would thank The Almighty for giving me strength to complete my report on time.

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INTRODUCTION

The adsorption is the process of accumulating substances that are in solution on a suitable interface. Adsorption is a mass transfer operation in that a constituent in liquid phase is transferred to the solid phase. The adsorbate is the substance that is being removed from the liquid phase at the interface. The adsorbent is the solid, liquid or gas phase on to which the adsorbate accumulates. The adsorption process has not been used extensively in waste water treatment, but demands for a better quality of treated waste water effluent, including toxicity reduction, have led to an intensive examination and use of the process of adsorption on activated carbon. Activated carbon treatment of waste water is usually thought of as a polishing process for water that has already received normal biological treatment. The carbon in this case is used to remove a portion of the remaining dissolved organic matter.

Many volatile organic compounds (VOCs) are toxic, posing a high risk to human health as a result of their widespread use and occurrence in workplace environments. Reducing the amount of organic vapours in ambient air is, therefore, an important task.

Activated carbons are the most versatile and frequently used adsorbents, and fixed beds of activated carbon, in the form of canisters or filters, are widely used for purifying contaminated air. Its large internal surface area and pore volume, its ability to absorb most organic vapours and low cost make activated carbon one of the most practical adsorbents.

Activated carbon beds eventually become exhausted after continuous exposure to air contaminated with organic vapours. The time at which an organic vapour of a defined concentration is able to penetrate the bed is known as the breakthrough time of the adsorbate. In practical situations, a key factor is the service life of the filter. This is defined as the time at which the concentration of the compound penetrating the filter reaches an unacceptable level. An accurate estimate of this service life is of great importance to both users and manufacturers. A predictive model for filter performance would reduce the need for time consuming filter tests, aid in the design of filters with optimized

performance and provide knowledge of the service life of military filters exposed to conditions and chemicals encountered in civilian situations.

ACTIVATED CARBON

Activated carbon is a solid, porous, black carbonaceous material. It is distinguished from elemental carbon by the absence of both impurities and an oxidized surface. It can be prepared from a large number of sources such as coconut, wood, peat, coal, tar, sawdust, and cellulose residues. Any carbon source can be converted into activated carbon via a number of methods. Usually, the process is divided into carbonization and activation. During carbonization most of the non-carbon elements are removed in gaseous form by the pyrolytic decomposition of the source material. The porous structure is mainly developed during activation by means of an activation agent that reacts with the carbon. Such agents may include synthetic acids, bases, and other substances in a stream of activating gases such as steam (H₂O), nitrogen (N₂) or carbon dioxide (CO₂).

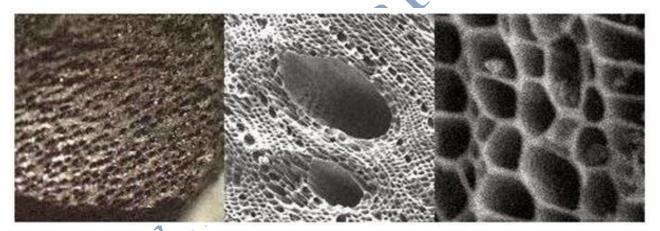


Fig.1: Activated carbon: surface and pores – scanning electron microscope image.

Magnification increases from left to right

Activated carbon has an extraordinarily large surface area and pore volume, making it suitable for a wide range of applications. It can be used as a decolorizing agent, a taste and

odour removing agent or as a purification agent in food processing. One major use of activated carbon is in water purification, including the production of potable water and the treatment of waste and ground waters.

The most important property of activated carbon, the property that determines its usage, is the pore structure. The total number of pores, their shape and size determine the

adsorption capacity and even the dynamic adsorption rate of the activated carbon. IUPAC classifies pores as follows:

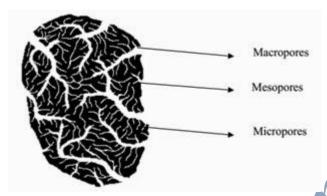
 $\begin{aligned} & macropores: \ d_0 > 50nm \\ & mesopores: \ 2 \leq d_0 \leq 50nm \end{aligned}$

micropores: $d_0 < 2nm$

ultramicropores: $d_0 < 0.7$ nm

supermicropores: $0.7 < d_0 < 2nm$

where d_0 is the pore width for slit type pores or the pore diameter for cylindrical pores



The macropores act as transport pathways, through which the adsorptive molecules travel to the mesopores, from where they finally enter the micropores. The micropores usually constitute the largest proportion of the internal surface of the activated carbon and contribute most to the total pore volume. Most of the adsorption of gaseous adsorptives takes place within these micropores, where the attractive forces are enhanced and the pores are filled at low relative pressures. Thus, the total pore volume and the pore size distribution determine the adsorption capacity.

TYPES OF ACTIVATED CARBON

Powdered Activated Carbon

PAC for water treatment: The feed location

of PAC can be at any point prior to filtration. The most common locations are in the flash mixer or flocculator since these pieces of equipment will mix the PAC into the water very well. However, some plants feed PAC just before filtration so that the PAC will form a layer on top of the filter and ensure that all water comes in contact with the activated carbon. Adding PAC just before filtration can cause problems, though, since the small PAC particles can pass through the filters and cause dirty water complaints from customers or can cake filters and result in reduced filter runs. Powdered activated carbon, or PAC, is a form of activated carbon with a very small particle size. Treatment involves adding PAC to water, allowing the PAC to interact with contaminants in the water, then removing the PAC by sedimentation or filtration.

Regardless of the feed location, PAC can be added to water using either a dry feeder or as slurry. Dry feeders are most often used in small plants when PAC is fed at intervals in response to periodic taste and odour problems. In contrast, slurries (mixtures of PAC with water) are used in larger plants or when PAC is fed continuously. Since it is difficult to make the PAC mix with water, the mixer should have an overhead spray system.

The effectiveness of PAC in adsorbing tastes and odours depends on adequate mixing, contact time, dosage, and on the cause and concentration of the taste/odour problem. Mixing and contact time are determined by the location at which the PAC is added in the treatment process, so adjustments made by the operator will usually involve only dosage adjustments. The dosage usually ranges from 1 to 15 mg/L but must be much higher, in the range of 100 mg/L or more, when the PAC is being used to remove trihalomethanes or trihalomethane precursors. The operator chooses an appropriate dosage using jar tests and the results from odour and taste tests.

Granular Activated Carbon

Granular activated carbon, also known as **GAC**, has a larger particle size than PAC with an associated greater surface area. Like PAC, GAC can remove trihalomethane precursors as well as taste and odour compounds.

APPLICATION OF ACTIVATED CARBON

GAC is used as a filter medium, either as a layer in a rapid-sand filter or in a separate filter known as a **contactor**. When contactors are used, the contactor is placed downstream of the filter so that turbidity won't clog the contactor.

Although GAC filters can be operated like a rapid sand filter in most ways, backwashing and surface washing are not the only cleaning required for the units. The entire surface of the GAC will eventually become covered with contaminants, just as a softener's resin will become covered with magnesium and calcium ions. A GAC filter can typically operate for months or years before reaching this state, depending on the contaminant levels in the influent water. Once the GAC has reached its adsorption capacity, it must be regenerated using the same heating process used to activate the carbon.

Carbon adsorption is used principally for the removal of refractory organic compounds, as well as residual amounts of inorganic compounds such as nitrogen, sulphides and heavy metals. The removal of taste and odour compounds from waste water is another important application, especially in reuse applications. Both powdered and granular activated carbon are used and appears to have low adsorption affinity for low molecular weight polar organic species. Typical compounds that can be removed by carbon adsorption are given in the table.

States	Purpose	Applications	Examples
	Recovery	Gasoline Vapour Recovery	Gasoline Fuel recovery, ELCD
		Solvent Recovery	MEK, Cyclohexanone, CS ₂ , Furon, Trichloroethane
Gas Phase	Odour Removal	Room Odour Removal	Tobacco, CO, Room filters, Toilet Odour, Pet Odour
j		Refrigerator	Deodourizer
Ì		Automobile Cabin air fi	Cabin air filters
Ì		Tobacco	Cigarette Filter
Ì		Hospital	Anaesthetic gas removal
Ì		Ozone Removal	Copiers, Laser Printers
	Harmful Gas	Closed Environment	Dioxin removal, Space Ships, Underground CO2

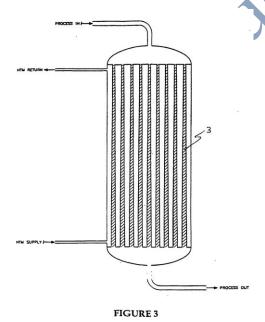
	Gas Separation	Nitrogen PSA	Nitrogen Gas Separation
		Other PSA	Radio Active Gas
Liquid Phase Table 1: application of activated carbon	Water Treatment	Factory Waste Water	Cleaning Waste Water
		Drinking Water Treatment	Trihalomethane, Chlorid VOCs, Lead, Arsenate removal
	Decolourization of Industrial Chemicals	Industrial Use	Sugar refinement, Pharmaceutical use, Whisky distilment
	Medical Applications	Medical and Nursing	Kidney machine, Nursir supplies, Respirators
	Electronics	Electrodes	Double Layer Capacitor Hardisks
	Mineral Recovery	Gold Recovery	Gold Recovery

ACTIVATED CARBON ADSOPTION SYSTEMS

Fixed bed type

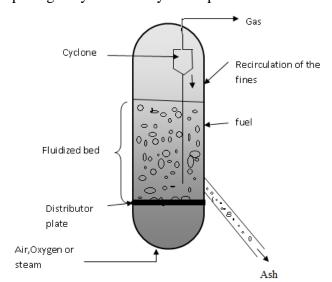
A fixed bed column is used commonly for contacting waste water with GAC. Fixed bed columns can be operated singly, in series or in parallel. Granular medium filters are commonly used upstream of the activated carbon contractors to remove the organics associated with the suspended solids present in secondary effluent. The water to be treated is applied to top of the column and withdrawn at bottom. The carbon is held in place with an under drain system at the bottom of column. Provision for backwashing and surface washing is often provided in waste water applications to limit the head loss build-up due to the removal of particulate suspended solids within the carbon column.

The advantage of down flow design is that adsorption of organics and filtration of suspended solids is accomplished in a single step. Although upflow fixed bed reactors have been used, down flow beds are used more commonly to lessen the chance of accumulating particulate matter in the bottom of the bed, where the particulate matter would be difficult to remove by backwashing. If soluble particles are not maintained at a high level, more frequent regeneration of carbon may be required.



Xpanded bed type

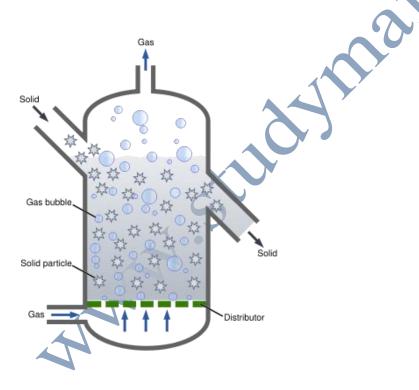
Expanded bed, moving bed and pulsed-bed carbon contactors have also been developed to overcome the problems associated with head loss build-up. In expanded bed system, the influent is introduced at the bottom of the column and the activated carbon is allowed to expand, much as a filter bed expands during backwash. When the adsorptive capacity of activated carbon is exhausted, the bottom portion of carbon is removed, and an equivalent amount of regenerated or virgin carbon is added to the top of the column. In such a system, expanded-bed upflow contractors may have more carbon fines in the effluent than down flow contractors because bed expansion leads to the creation of fines as the carbon particles collide and abrade, and allows the fines to escape through passageways created by the expanded bed.



Fluidized bed reactor type

A fluidized bed reactor (FBR) is a type of reactor device that can be used to carry out a variety of multiphase chemical reactions. In this type of reactor, a fluid (gas or liquid) is passed through a granular activated carbon at high enough velocities to suspend the solid and cause it to behave as though it were a fluid. This process, known as fluidization, imparts many important advantages to the FBR. As a result, the fluidized bed reactor is now used in many industrial applications.

The solid substrate (activated carbon) material in the fluidized bed reactor is typically supported by a porous plate, known as a distributor. The fluid is then forced through the distributor up through the activated carbon. At lower fluid velocities, the solids remain in place as the fluid passes through the voids in the material. This is known as a packed bed reactor. As the fluid velocity is increased, the reactor will reach a stage where the force of the fluid on the solids is enough to balance the weight of the solid material. This stage is known as incipient fluidization and occurs at this minimum fluidization velocity. Once this minimum velocity is surpassed, the contents of the reactor bed begin to expand and swirl around much like an agitated tank or boiling pot of water. The reactor is now a fluidized bed. Depending on the operating conditions and properties of solid phase various flow regimes can be observed in this reactor.



ADSORPTION ISOTHERM

The quantity of adsorbate that can be taken up by an adsorbent is a function of both the characteristics and concentration of adsorbate and the temperature. The characteristics of the adsorbate that are of importance include: solubility, molecular structure, molecular weight, polarity, and hydrocarbon saturation. Generally, the amount of material adsorbed is determined as a function of the concentration at a constant temperature, and the resulting function is called an adsorption isotherm. Adsorption isotherms are developed by exposing a given amount of adsorbate in a fixed volume of liquid to varying amounts of activated carbon. Typically more than ten containers are used, and the minimum time allowed for the samples to equilibrate where powdered activated carbon is used in seven days. If granular activated carbon is used, it is usually powdered to minimize adsorption times. At the end of the test period, the amount of absorbate remaining in solution is measured. The adsorbate phase concentration data computed using the equation, are then used to develop adsorption isotherms.

$$q_e = [(C_0 \cdot C_e)/m] V$$

where,

q_e = adsorbent phase concentration after equilibrium, mg adsorbate/ g adsorbent

 C_0 = initial concentration of adsorbate, mg/L

C_e = final concentration of adsorbate after absorption has occurred, mg/L

V = volume of liquid in the reactor, L

m = mass of adsorbent, g

Laboratory evaluation of the adsorption isotherm and the adsorption capacity is time consuming and may be affected by toxicity or the availability of the adsorbate. For such difficult cases, a model that can predict the adsorption capacity, making testing unnecessary, would be highly desirable. A number of such models have been proposed for the adsorption isotherm: the Freundlich isotherm equation; the Langmuir isotherm; BET-theory; the Hacskaylo and Levan equation; the Dubinin Raduskevish equation; and a modification of the DR equation developed by Stoeckli.

Dubinin Raduskevish Equation

Among the existing predictive equations, the DR equation has been the most widely used to predict organic vapour adsorption onto activated carbon. It has several advantages:

- a) there is a good data fit over a wide concentration range
- b) temperature is included as a parameter
- c) it is built around physical parameters
- d) it is easy to apply.

Dubinin postulated that the amount of vapour adsorbed (W) by an activated carbon source, at a relative pressure (P/Ps), is a function of the thermodynamic potential (A with A expressed as

$$A = RT \ln (Ps/P)$$

where R is the universal gas constant, T is the absolute temperature, Ps is the saturated vapour pressure at temperature T, and P is the partial pressure of the adsorbate.

By examining the adsorption of simple organic compounds, such as benzene, Dubinin concluded that the function was Gaussian. This led to the classical expression of Dubinin and Radushkevich (the D-R equation):

$$W = W_0 * \exp(A/\beta E_0)2$$

Where, W_0 is the maximum amount adsorbed, E_0 is the characteristic adsorption energy for a reference vapour on a specific adsorbent. The parameter β is called the affinity coefficient or similarity coefficient, and expresses the ratio of the characteristic free energies of adsorption for the test and reference vapours. Benzene is, by convention, used as the reference compound for carbonaceous materials, and is, by definition, given the value $\beta=1$.

Freundlich Isotherm

The Freundlich isotherm is used most commonly to describe the adsorption characteristics of the activated carbon used in water and waste water treatment. It was derived in 1912 and is defined as follows:

$$x/m = K_f C_e^{\ 1/n}$$

Where, x/m is the mass of adsorbate adsorbed per unit mass of adsorbent, mg adsorbate/g activated carbon

 K_f = Freundlich capacity factor, (mg absorbate/ g activated carbon)

C_e = equilibrium concentration of adsorbate in solution after adsorption, mg/L

1/n = Freundlich intensity parameter

Langmuir Isotherm

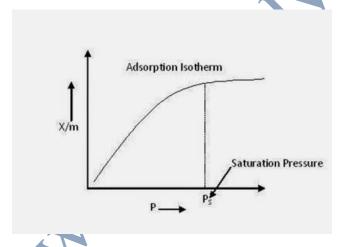
Langmuir adsorption isotherm is derived by assuming: (1) a fixed number of accessible sites are available on the adsorption surface, all of which have the same energy, and (2) adsorption is reversible. Equilibrium is reached when the rate of adsorption of molecules on to the surface is same as the rate of desorption of molecules from the surface. The rate at which adsorption proceedes is proportional to the driving force, which is difference between the amount adsorbed at a particular concentration and the amount can be adsorbed at that concentration. At the equilibrium concentration, this difference is zero. Langmuir adsorption isotherm can be expressed as:

$$x/m = (abCe)/(1+bCe)$$

x/m = mass of adsorbate adsorbed per unit mass of adsorbent, mg adsorbate/g activated carbon

a, b = empirical constants

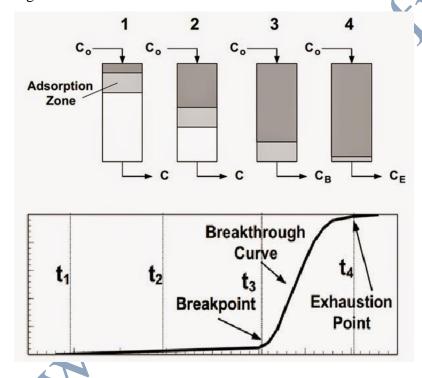
Ce = equilibrium concentration of adsorbate in solution after adsorption, mg/L



Adsorption isotherm

ADSORPTION KINETICS

Initially, when a contaminated gas stream passes through a packed carbon bed, most of the contaminant, the adsorbate, is adsorbed in the vicinity of the inlet to the bed. The gas then passes on with little further adsorption taking place. Later, when the inlet part of the adsorbent becomes saturated, adsorption takes place deeper inside the bed. As more gas passes through and adsorption proceeds, the so-called mass transfer zone (MTZ) moves forward until the breakthrough point is reached. If the flow of gas is continued, the exit concentration from the bed will rise gradually until it reaches the level of the inlet concentration. At this point, the bed is fully saturated. The service life of the filter bed is regarded as the time when the exit concentration has reached an unacceptable level.



Adsorption kinetics

Several models to predict the breakthrough curves for physisorption of organic vapours have been proposed. Among these, the Wheeler-Jonas equation is the most widely used to estimate the breakthrough time of organic compounds on activated carbon. It has a

simple form, with some parameters readily available from the literature or from carbon manufacturers, and it is known to yield good predictions for breakthrough times. It has recently been shown that the Wheeler-Jonas equation has a wider scope of application than just physisorption for a constant flow pattern.

The Wheeler-Jonas equation takes the form

$$t_b = \frac{W_e W}{C_0 Q} - \frac{W_e \rho_B}{k_v C_0} \ln \left[\frac{(C_0 - C_x)}{C_x} \right]$$

where

 t_b = time to reach the breakthrough fraction $b = C_x / C_0$ (min)

 C_0 = bed inlet concentration (g/cm³)

 C_x = chosen breakthrough concentration (g/cm³)

W = weight of the carbon bed (g carbon)

 W_e = equilibrium adsorption capacity of the carbon for a given vapour (g/g carbon)

Q = volumetric flow rate (cm³/min)

 ρ_B = bulk density of the carbon bed (g carbon/cm³)

 k_v = overall adsorption rate coefficient (min⁻¹)

To use this equation, two parameters, W_e and k_v , must be determined. This can be done either experimentally or by extrapolation from measurements using a reference adsorbate. The first parameter W_e , the adsorption capacity, is usually calculated from an adsorption isotherm equation; the Dubinin-Radushkevich equation is often used in the case of

organic vapour adsorption.

ADVANTAGES OF ACTIVATED CARBON ADSORPTION Highly effective at removing non-polar organic chemicals from water. Applicable to a wide variety of organic compounds Very effective at removing colours from waste streams. Effective at removing low levels (ppb range) of inorganic pollutants. Thermal regeneration of the carbon destroys the adsorbed waste solute. Very flexible system allows rapid start-up and shut down as needed. System can be designed so that it is portable, to be taken to waste sites. LIMITATIONS OF ACTIVATED CARBON ADSORPTION Limited to wastes with low organic concentrations (<5%). Limited to wastes with very low inorganic concentrations (< 1%). Unable to remove highly soluble organics, or those with low molecular weights. Systems cannot tolerate suspended solids in the influent stream (due to clogging). High operating costs due to carbon costs system requirements. Disposal of contaminated carbon can be problematic if it is not regenerated.

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