REMOVAL OF CARBOXYLIC ACID FROM WASTE WATER USING ADSORBENTS

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF ENGINEERING
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

By

VIVEK KUMAR

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF ROORKEE
ROORKEE-247667 (INDIA)

JANUARY, 1994

CANDIDATE'S DECLARATION

I here by declare that the work which is being presented in the dissertation entitled "**REMOVAL OF CARBOXYLIC ACID FROM WASTE WATER USING ADSORBENTS**", in partial fulfilment of the requirement for the award of the degree of *MASTER OF ENGINEERING IN CHEMICAL ENGINEERING WITH* SPECIALIZATION IN INDUSTRIAL POLLUTION ABATEMENT, Submitted in the Department of Chemical Engineering, University of Roorkee, Roorkee, is an authentic record of my own work carried out from June 1993 to Jan. 1994 under the kind supervision of *Shri C.B.Majumdar, Lecturer,* Deptt of Chemical Engineering, University of Roorkee, Roorkee.

The matter embodied in this dissertation has not been submitted by me for the award of any other degree.

(VIVEK KUMAR)

DATED JAN. 31st **,1994**

ROORKEE

This is certified that the above statement made by the candidate is correct to the best of our knowledge.

(SHRI C.B. MAJUMDAR)
Lecturer
Deptt. of Chemical Engineering
University of Roorkee
Roorkee

ACKNOWLEDGEMENT

I take this opportunity to express my deep sense of gratitude and sincere thanks to my supervisor *Shri. C.B.Majumdar,* Lecturer, Department of Chemical Engineering, University of Roorkee, Roorkee. This work has been possible due to his inspirational guidance, and painstaking involvement.

I am grateful to Dr. I.M.Mishra, Head of Chemical Engineering Department and Dr. Shri Chand, Lecturer, Chemical Engineering Department for their kind co-operation, inspiration and deep involvement.

I thank all the Laboratory staff and CAD Centre staff for their excellent Co-operation during the experimental phase of this work.

I would like to thank all my friends specially Vivek, Girraj, Amrendra, Harkhush , Sarbjeet for their numerous and valuable contribution to this dissertation.

Finally, I pay my heartiest regards to Shri Y.Kumar, Scientist, I.I.P. Dehradun, my parents and friends Manish , Ajay and Aman for their blessings, love and moral support which always gave me courage and confidence in compeletion of this dissertation.

(VIVEK KUMAR)

ABSTRACT

In recent years, as waste water effluent quality standards become more stringent, the method used to insure that effluent quality becomes increasingly sophosticated. Physical-Chemical methods now complement and supplant biological treatment. As a result of this people have become more attuned to what is the specific species of pollutant as opposed to what is its B.O.D. or T.O.C.

With this new awareness of chemical species identification, the realization that industrial waste contain large amounts refractory organic compounds have occured. Typical refractories are acetone, formaldehyde and various carboxylic acid, (especially acetic acid). Corboxylic acids are major commercial chemicals and are potentially even more important as inter mediates and products from fermentation of bio mass. They have wide application in chemicals, man made fibres, dyestuffs, drugs, food industry and many more.

Carboxylic acid are skin irritant, toxic and they also causes irritation of mucous membrane. Besides these environmental reasonsa wide gap between demand and supply of these acids also make to think about removal aswell as recovery of acids. Few techniques such as chemical treatment, distillation, extraction, biological treatment, adsorption are there which can be used for carboxylic acids removal.

Unfortunately till now not much attention has been paid towards the treatment of effluent containing carboxylic acids. Moreover, whatever work has been done that is on the treatment of effluent containing carboxylic acids by means of extraction or adsorption by conventional adsorbents.

In the present study we have undertaken adsorption studies using cheap agricultural waste materials as adsorbents, namely activated bagasse carbon, activated coconut jute, activated sawdust, activated rice husk. The experiments were conducted in a batch apparatus and effects of the variables, such as, initial acid concentration, adsorbent dose, time and temperature were studied. Effect of adsorbent dose on the removal of C.O.D. was also studied.

For the studies acetic acid has been used as a proto type carboxylic acid as acetic acid is one of most important commercial member of large carboxylic acids family .

For the studies a synthetic waste water was prepared using acetic acid in redistilled water. Then firstly equillibrium time was calculated for all the adsorbents. After that effects of all the variable were studied.The results indicated that acid could be satisfactorly removed from the waste water using these adsorbents. Among of the adsorbents studied activated bagasse carbon was found to be the most satisfactory. The kinetics of the adsorption process was also studied.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

CHAPTER 1

INTRODUCTION

(1) GENERAL

Healthy environment is the most essential prequisite of human life. Today environmental pollution is a great challange before the world. It is neither compromisable nor can be shifted from the top priority of the problems. It has no alternative other than to control as effeciently as possible.

Having stolen the fire from the God's, according to the classic myth, premetheus-man-has made the most of it. As now we stand in fear and trepidation, as we confront the awe some consequences and possibilities of what we used to view as our ever growing sovergein power over God's creation or to shift our imagery to Biblical core. Having plucked marvelously varied fruits from the tree of knowledge, we have begin to wonder if the tree of life is with in the gates of paradise, instead of moving closer with in our reach is for ever receding so that not only life eternal but the jolt of life as such may slip from us. Mankind at the height of its triumph. paradoxically finds itself stymied and at bay. Far as has aptly been observed, our most triumphant success threaten to back fire. Many solution has become the problem.

What has happened is that over quite a period of time man for all the continuing struggle to earn his daily bread by teeming milllion - **"No longer lives almost overwhelmed by the scale of his natural environment."** It is the enviranment that is begining to be over whelmed by man.

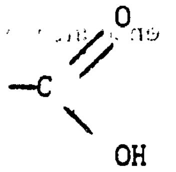
A rapid pace of Industrialization coupled with uncontrolled exploitation of nature, has caused continuous dumping of industrial by-products, hazardous chemicals and nuclear wastes, deforestation in vast area of the earth and pollution of the river basins, lakes and seas. The advanced technologies and improved facilities in the developed countries and their full fledged and successful implementation has forced the developing countries such as India, which is still in an early stage of industrialization, but its harmful effects on the environment have already started showing signs, to focus their attention towards the most effective treatment process so that the pollutant discharged from various sources may be brought to the safe disposal limits.

(2) WATER POLLUTION

Advance in chemical engineering have bought ever increasing compounds in waste water streams both as rejected by products of industrial process and as residues of common commercial products. This has resulted in the degradation of quality of recieving bodies of water and land there by impairing use. Carboxylic acids are already major commercial chemicals and are potentially even more important as intermediates and products from fermentation of bio mass. The effluent from wood pulping plant, refinery, petrochemical industry, dyestuffs, drugs and food industry contain carboxylic acids.

(3) CARBOXYLIC ACIDS

Of the organic compunds that show appreciable acidity, by far the most important are the carboxylic acids. These compounds contain the carboxyl group.



attached to either an alkyl group (RCOOH) and aryl group (Ar COOH) (Table1.1)[1]

Whether the group is aliphatic or aromatic, saturated or unsaturatd, substituted on unsubstituted, the properties of the carboxyl group are essentially the same.

3.1. PHYSICAL PROPERTIES

Carboxylic acid molecules are polar and can form hydrogen bonds with each other and with other kinds of molecules. In the aliphatic acids the first four acid are miscible with water, the five carbon acid is partly soluble and the higher acids are virtually insoluble.

The simplest aromatic acid, benzoic acid, contains too many carbon atoms to show appreciable solubility in water. Carboxylic acid are soluble in less polar solvents like either alcohol, benzene ets.

The odors of the lower aliphatic acids progress from the sharp, irritating odors of formic and acetic acids to the distinctly unpleasant odors of butyric, valeric and caproic acids, the higher acid have little odor beacuse of their low volatility.

(4) SIGNIFICANCE

Carboxylic acids are skin irritant toxic carcinogenic and mutagenic to human being and animals. These acids cause burn. Inhalation of these acids caused irritation of mucous membrane. Besides these environmental reason a wide gap between demand and supply of acid also made to think about recovery of acids.

The carboxylic acids are usually encountered in relatively dilute, and often complex, aqueous solution.

The most common problem of organic acid removal involves separation from these dilute effluent. Although further dilution and biological treatment could be the alternatives treatment methods for safe disposal. But recovery of acids is not possible from these methods Besides this they may also lead the problem of disposal over loading. Adsorption is an attractive recovery method for dilute solutions.

Unfortunately uptill not much attention has been paid towards the treatment of effluent containiing carboxylic acids. Moreover, what ever work has been done that is on the treatment of effluent containing carboxylic acids by means of extraction or adsorption by conventional adsorbents. In the present study we have under taken adsorption studies using cheap agricultural waste material as adsorbents, namely activated bagasse carbon, corbonised, activated coconut jute, activated saw dust, activated rice husk. For the studies acetic acid has been used as a proto type carboxylic acid, as acetic acid is of the most important commercially used member of large carboxylic acids family containing as many as 35 members.

CHAPTER II

TABLE 11

Formula	Name			m. p., °C	b. p.$_{760}$ °C	Density d_4^{20}	Dissociation constant at 25°C, K_a	pK_a (at 25°C)
	trivial	Geneva	carboxylic system					
$H-COOH$	Formic	Methanoic	—	8.40	100.7	1.220	1.77×10^{-4} (at 20°C)	3.75 (at 20°C)
CH_3-COOH	Acetic	Ethanoic	Methanecarboxylic	16.6	118.1	1.049	1.76×10^{-5}	4.75
CH_3-CH_2-COOH	Propionic	Propanoic	Ethanecarboxylic	—22.0	141.1	0.992	1.34×10^{-5}	4.87
$CH_3-CH_2-CH_2-COOH$	Butyric	Butanoic	1-Propanecarboxylic	—7.9	163.5 (at 757 mm Hg)	0.9587	1.54×10^{-5} (at 20°C)	4.81
$CH_3-\underset{\mid}{CH}-COOH$ CH_3	Isobutyric	2-Methylpropanoic	2-Propanecarboxylic	—47.0	154.4	0.949	1.44×10^{-5} (at 18°C)	4.84
$CH_3-CH_2-CH_2-CH_2-COOH$	Valeric	Pentanoic	1-Butanecarboxylic	—59; —34.5	187.0	0.942	1.51×10^{-5} (at 18°C)	4.82
$CH_3-\underset{\mid}{CH}-CH_2-COOH$ CH_3	Isovaleric	3-Methylbutanoic	1-Isobutanecarboxylic	—37.6	176.7	0.937 (d_4^{15})	1.70×10^{-5}	4.77
$CH_3-(CH_2)_4-COOH$	Caproic	Hexanoic	1-Pentanecarboxylic	—1.5 to —2.0	205	0.929	1.31×10^{-5}	4.88
$CH_3-(CH_2)_5-COOH$	Enanthic	Heptoic	1-Hexanecarboxylic	—10.0	223.5	0.918	1.28×10^{-5}	4.89
$CH_3-(CH_2)_6-COOH$	Caprylic	Octanoic	1-Heptanecarboxylic	+16.0	237.5	0.910	1.28×10^{-5}	4.89
$CH_3-(CH_2)_7-COOH$	Pelargonic	Nonanoic	1-Octanecarboxylic	12.0	254	0.9055		—
$CH_3-(CH_2)_{14}-COOH$	Palmitic	Hexadecanoic	1-Pentadecanecarboxylic	64.0	271 (at 100 mm Hg) 339-356 (decomp.)	0.8530 (at 62°C)	—	—
$CH_3-(CH_2)_{15}-COOH$	Margaric	Heptadecanoic	1-Hexadecanecarboxylic	60.6	227 (at 100 mm Hg)	0.8578 (d_4^{60})	—	—
$CH_3-(CH_2)_{16}-COOH$	Stearic	Octanedecanoic	1-Heptadecanecarboxylic	69.4	291 (at 100 mm Hg)	0.847 (at 69°C)	—	—
$CH_3-(CH_2)_{24}-COOH$	Cerotic	Hexacosanoic	Pentacosanecarboxylic	87.7	Decomposes	0.8360 (at 79°C)	—	—

---

* This table does not cover all isomers, and only selected homologues are given.

CAPTER 2

LITERATURE REVIEW

2.1 SOURCES & SIGNIFICANCE

Carboxylic acids are used as plant growth regulators herbicides and fungicides. They are also naturally occurring substance which could find their way into water (from fruits, leaves, dead animals).

Very few information such as D.M.T. plant waste contains mainly acetic acid upto 1-3% with small quantity of formic acid and methanol are available about the effluent containing carboxylic acid. The effluent from wood pulping plant, refinery, petrochemical industry, also contains carboxylic acids. Acetic acid has wide application in chemicals, man made fibres, dye stuffs, drugs and food industry (Table 2.1)[4].

TABLE 2.1

ACETIC ACID PRODUCTS AND THEIR END APPLICATIONS

Product	End Use
Vinyl acetate	Latexpaints and finishes (water based), plastics adhesives, PVA melt adhesives
Acetic anhydride	Rayon and cellulose acetate (for sheeting, film, fabrics and lacquers)
Acetamide and its derivatives	Cosmetics and pharmaceuticals, insecticides and synthesis of pigments.
Deimethyl acetamide	Solvent for polar/non polar compunds, some plastics and unsaturated hydrocarbons.
Acetenilide	Pharmaceuticals and dyes.
Chloroacetic acids	Production of herbicides, carboxymethyl cellulose and thiocyanate insecticides.

Carboxylic acids are skin irritant toxic carcinogenic and mutagenic to human beings and animals. Acetic acid causes burn inhalation of acetic acid caused irritation of mucous membrance. Besides these environmental reason a wide gap between demand and supply of acetic acid also made to think about recovery of acid.

TABLE 2.2

DEMAND - SUPPLY GAP OF ACETIC ACID	('000 Tonnes)
Demand	322.0
Availability*	212.4
Gap (-)	(-) 109.6

* Assuming 100% capacity utilisation

2.2 VARIOUS REMOVAL AND RECOVERY METHODS

The most common problem of organic acid removal involves separation from very dilute effluent. Further dilution and biodegradation can be the economic alternatives to remove organic acid but they may lead the problem of disposal over loading.

Four alternative organic acid removal/recovery processes are generally considered :

2.2.1 CHEMICAL TREATMENT METHOD

In this treatment, acid is destructed by adding some chemicals. One of the such type of method is U.V. catalyzed chlorination. In this method destruction can be accomplished by chlorination in the presence of U.V. radiation. Mayer and parmele [8]. found that the following reaction occurred under more carefully controlled conditions.

$$CH_3COOH + Cl_2 \longrightarrow CH_3Cl + CO_2 + HCl$$

They developed the kinetics of this reaction and found it to be first order in acetic acid concentration, chloride ion and zero in chlorine. In the range 1-20 mg/l the reaction is inhibited above 20 mg/l Cl_2. The kinetics can be described by

$$\frac{dc}{dt} = K(C)$$

The reaction is highly dependent on pH, the ideal being between pH 3.5 and 4.5. U.V. radiation is needed with a wave length below 3600 A^o.

The overall process is shown in Fig. 2.1 The reactor is two well stirred tank in series, it has been that 90% of the acetic acid on the waste stream (1,400 - 1,800 mg/l acetic acid) can be removed with this scheme using 40 minute holding times in each rector. But there are various disadvantages associated with this method, as it is limited to waste streams with high chloride concentration and in this method acetic acid is destroyed, not recovered. The sage of other chemicals also makes it costly.

2.2.2 SIMPLE AND AZEOTRORPIC DISTILLATION

Distillation can be one of the method for organic acid recovery. In case of acetic acid recovery glacial acetic acid is recovered. The technique of distillation is well established. In azeotropic distillation some azeotropic agent such as ether are added insolution as these agents increase the volatility of water and their solubility in water is very low so they can be separated out easily from the condensed vapours. But recovery of organic acid using distillation for industrial effluewnt is not feasible as acid concentration is very low in these effluents.

2.2.3 SOLVENT EXTRACTION [8]

Another alternative for the treatment of acetic acid wastes is solvent extraction. The organic acid is extracted by contacting the solvent with the waste water. Recently many studies have been carried out on the extraction of organic acid from aqueous solutions using long chain alkylamines. A schematic diagram of a proposed process is shown in Fig. 2.2 However, use of solvents makes it sensitive in term of economic and industrial application.

2.2.4 ADSORPTION

Adsorption is well recognised as a unit operation for the removal of impurities present in dilute concentration from waste water, it has also added advantage of minimizing contamination and avoiding heating of the medium. At low concentration a complete removal or organic acid can be done by using adsorption as treatment method. Various adsorbent for organic acids adsorption are, activated charcoal, activated carbon and basic polymer sorbents etc. organic acid can be recovered by doing solvent regeneration of exhausted adsorbents. Various solvents as caustic soda, ethanol can be used for this purpose. Schematic diagram of adsorption and desorption processes is in Fig. 2.3

2.3 PREVIOUS WORKS

As far as the previous works concern not much published work is available on the adsorption of carboxylic acid. In this context three research papers are being discussed in brief under their respective titles.

2.3.1 ADSORPTION OF CARBOXYLIC AGROCHEMICALS FROM SALINE WATER BY CHARCOAL [6]

In this research batch adsorption study of organic pollutants containing carboxyl groups on activated charcoal is made. Distribution coefficient of organic acids in water containing varying concentration of Ca(II), Po(III), Mn(II), Na(I) and Zn(II) also have been determined. The final results obtained show that at lower concentration, acid under study are totally adsorbed. Experiment shows that charcoal has high adsorption capacity for acids such as Benzoic, Cinnamic, β-Naphthaleneacetic acid etc. and relatively low adsorption capacity for acids such as Acetic, Adipic, Citric etc.

2.3.2 THE USE OF BASIC POLYMER SORBENTS FOR THE RECOVERY OF ACETIC ACID FROM DILUTE AQUEOUS SOLUTION [7]

Measurements were made of uptakes of acetic acid and water from aqueous solution into basic polymer sorbents. Sorption equilibria were interpreted through a chemical complexation model yielding sorption affinities and saturation capacities for acetic acid. Bascity scales, such as PKa and gutmann donor Number (DN), based upon the monodic functional group chemistry were shown to explain the trends in sorption affinities. Solvent leaching was investigated as a means of regenerating the sorbents. It was found the regeneration can be improved by using solvents of high doncity. Aqueous ammonia proved to be effective for regeneration moderately strong base sorbents. This is summarised as follows :

The sorption mechanism for mono functional acid such as acetic acid is rationalized as a 1:1 complex formation with basic functional groups in the sorbent. Sorbents with functional groups which are not sufficiently spaced apart in the polymer matrix encounter base-weakening effects, leading to a lowering of their capacities for weak acids. Also, sorbents with base weakening cross linking agents can have lower sorption affinities for weak acids.

Various bascity scales were examined for predicting sorption affinity. The Gutmann donor number (DN) is a good parameter of sorption affinity. Determinations of apparent polymer PKa are also useful. Selectivity for acetic acid over water can be comprmised by both polymer swelling and filling of macro pores with bulk solution. Swelling and very high porosity are undesirable.

Solvent leaching with common volaitile solvents such as methanol is useful for receiving acetic acid from the weaker base sorbents. In case of stronger sorbents solvents of higher bascity can be used. Ammonium hydroxide can strip acetic acid sorbed on strong base sorbents, yielding an aqueous ammonium acetate solution of higher concentration than the initial, presorption aqueous acetic acid solution. Further ammonia can be volatilised from solution, leaving molecular acetic acid.

2.3.3. REMOVAL OF ACETIC ACID FROM WASTE WATER [8]

In this paper several methods of treating wastes containing acetic acid have been discussed. These methods include activated carbon treatment, U.V. catalyzed chlorination, and solvent extraction. The following matter is mainly related to adsorption.

The acetic acid, adsorbs on activated carbon has been well documented. However, the adsorption is poor compared to other larger organic compunds, e.g. phenol (< 10% Vs~ 20% organic weight/carbon weight). Since operatinoal cost are generally related directly to carbon consumption, there is need for emphasis on both the improvement of the adsorption characteristics of activated carbon and improvement of method of regeneration. Since the former is generally the purview of the manufacturers of activated carbon, this paper was concentrated on improvemethods of activated carbon regeneration.

It is concluded finally that regeneration of saturated acetic acid adsorption column can be done by the use of caustic soda for desorption of Ethanol as solvent. When caustic soda is used for desorption, sodium acetate is recovered as final product. In the system where ethanol used as a vapor phase solvent regenerate. The acetic acid and ethanol react to form ethyl acetate which is removed by the excess solvent.

2.4 ADSORPTION

2.4.1 ADSORPTION TECHNIQUES

Adsorption is a surface phenomenon in which a susbtance is transferred from the liquid on gas phase to the solid phase and is attached to the surface of solid. Depending upon the nature of the forces responsible for the adherence of the adsorbate molecule on the adsorbent surface the process is known as physical or chemical adsorption.

Physical adsorption is reversible and equilirium is attained rapidly. Molecules are attached to the adsorption surface by weak vanderwalls forces or some time due to some Pi interaction. Multilayer adsorption is possible with new layer forming on the top of the previously formed layer.

In chemical adsorption, bond are formed between adsorabte molecules and the solid surface through electron sharing. Desorption takes place only with difficulty. In most cases only one layer of adsorbate molecules is formed at the interface as further from the surface chemical interaction cannot be brought about. This type of adsorption occurs on the sides and corners of micro crystalliteson the adsorbent.

Both physical and chemical adsorption are exothermic in nature, the desorption being endothermic. The kinetic energy of the adsorbate molecules is converted into thermal energy during adsorption and vice-versa. Heat of adsorption gives a fairly good account of the nature of interaction at the surface. Adsorption is a unique unit operation in a number of respects. In some cases the separation performed involves the accomplishment of literally hundreds of theoretical transfer units. In others, the nature of the adsorbent allows the highly specific and selective removal of one species from a mixture, based on differences in molecular size, there would be practically impossible to accomplish by any other means.

2.4.2 ADSORBENTS

A. Nonpolar solids, where the adsorption is mainly physical

B. Polar solids, where the adsorption is chemical but no change inthe chemical structure of molecules or the surface occure

C. Chemical adsorbing surface, which adsorb the molecules and then release them after action, which may be either catalytic leaving the surface unchanged, or non catalytic requiring replacement of the surface atoms.

Adsorbents are generally used in cylindrical vessels through which the stream to be treated is passed. Adsorbents are used in application requiring from a few kilograms to as much as thousands of kg in one plant.

Various commercially available adsorbents are activated carbon, silica gel, activated alumina, molecular sieves, activated clays, basic polymer sorbents etc. Some of the major type of adsorbents are given in Table 4 [11].

TABLE 2.3

Composition	Internal porosity (%)	External void fraction (%)	Bullk dry density Kg/m^3	Specific Surface area m^2/g
Acid treated clay	Ca30	Ca40	560-880	100-300
Activated alumina and bauxite	30-40	40-50	720-880	200-300
Alumina silicate	45-55	Ca35	660-705	600-700
Bone char	50-55	18-20	640	Ca100
Carbons	5-77	35-40	160-480	600-1400
Iron oxide Fe O	22	37	1440	130-250
Magnesia (MgO)	Ca75	Ca45	Ca400	20
Silica gel	Ca70	Ca40	Ca400	200
fuller's earth	50-55	Ca40	480-660	Ca320

In genral particle size, surface area per unit weight, pore size and their distribution are impportant from the adsorption point of view.

The pore size vary considerably from adsorbent to adsorbent. Activated carbons, activated alumina and silica gel do not possess an ordered crystal structure and consequently the pores are nonuniform. The distribution of the pore diameter within the adsorbent particles may be narrow (20 - 50 A^{o}) or it may range widely (20 - several thousand A^{o}) depending upon the adsorbent. Hence most molecular species, with the possible exception of high molecular weight polymeric materials, may enter the pores. Zeolite molecular sieves have pore of uniform size which are uniquely determined by the structure and chemistry of the crystal. Thus pores will completely exclude moleculas which are larger than their diameter. The zeolite composition available commercially have pore size which cover ranging from 3 to 10 A^{o}. Low temperature adsorption of inert gases may provide information about the shape and dimensions of the pores present in the matrix. The adsorption of nitrogen at low temperature on porous and nonporous solid, and the influence of such adsorption on capillary condensation and evaporation, are those concepts which help to calculate pore size distribution.

Most of the methods for the determination of the specific surface area of a adsorbent are based on the adsorption of substances on this surface. One of the methods used most frequently at the moment is based on the adsorption of inert gases, such as nitrogen or oxygen.

Activated carbon is a popular adsorbent widely used in water and waste treatment and several other applications. Commercially it is available in two forns, i.e. granular and powdered. Activated carbon in powder form having a high specific surface has greater affinity for various substances. The contact time required is also less as the surface is more exposed to the sulution. However, separation of carbon from solution after absorption is a major bottleneck with granular carbon although the contact time is high but separation is relatively easier.

Activated carbon are prepared from coal, charcoal or other carbonized materials by a process of activation nearly always this process amounts to a partial oxidation, conducted in such a way that the desired pore size structure is obtained.

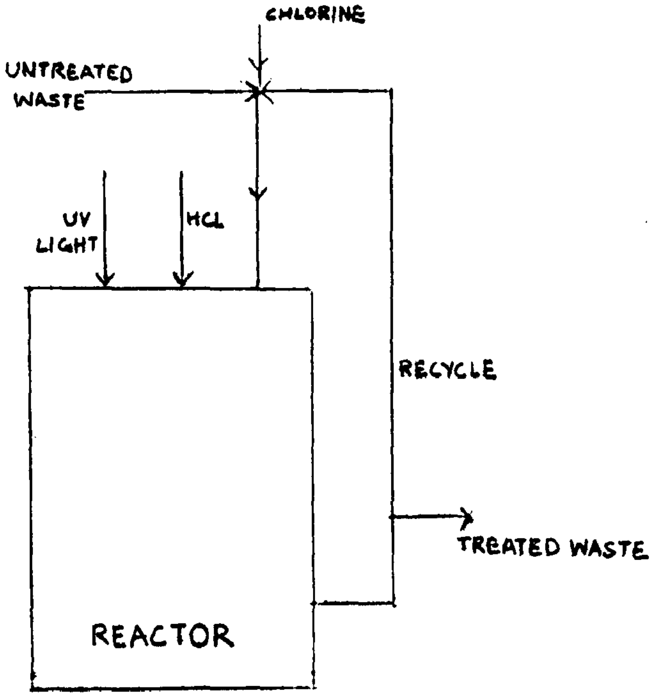
Activated alumina is prepared mostly by a thermmal dehydration procedure. Activated alumina is not pure Al_2O_3 but contains depending upon temperature and water vapour pressure, from a few tenth to about 5% water. Depending on prepartive conditions, other components may be present too, e.g. alkali oxide, ironoxide and sulphate. Activated alumina adsorbs water, as hydroxyl ions or as water molecules on the surface, depending upon the temperature. Alumina has heterogenious surface. Lewis acid sites on the surface of alumina, core considered to be the active centres for a great number of catalytic reaction. But from variouos other models it must be concluded that also pair and triple oxide defects occur, which can be expected to behave as basic, electron donation centres.

Silica gel is one of the various forms of amorphous silica. Other forms are nonporous precipitates, silical porous, and pyrogenic materials like aerosol the mineral opal et al. The usual methods of perparation are precipitated with acids from silicate solutions on silicon derivatives such as silicon tetrachloride or tetraethoxysilcon Si $(OC_2H_5)_4$. Amorphous silica is a system of polycondensed units of elementary particles, whose size and packing determine the geometrical structure or texture. Irrespective of dispersity of the silica, the elementary particle consists of a SiO_4 network, at the surface of the tetrahedral configuration of silicon is maintained by hydroxyl groups.

LOW COST ADSORBENTS :

A veriety of low cost materials produced as wastes from various minerals and process industries themselves have been proved good adsorbents for waste treatment. Though they are oftenly lesser efficient but a compromise is always to be reached between the cost saving and reduce efficiency. Various low cost adsorbents are, wood bark, rice husk, cotton waste, carbonized wool etc.

FIG 2.1 - UV CHLORINATION PROCESS



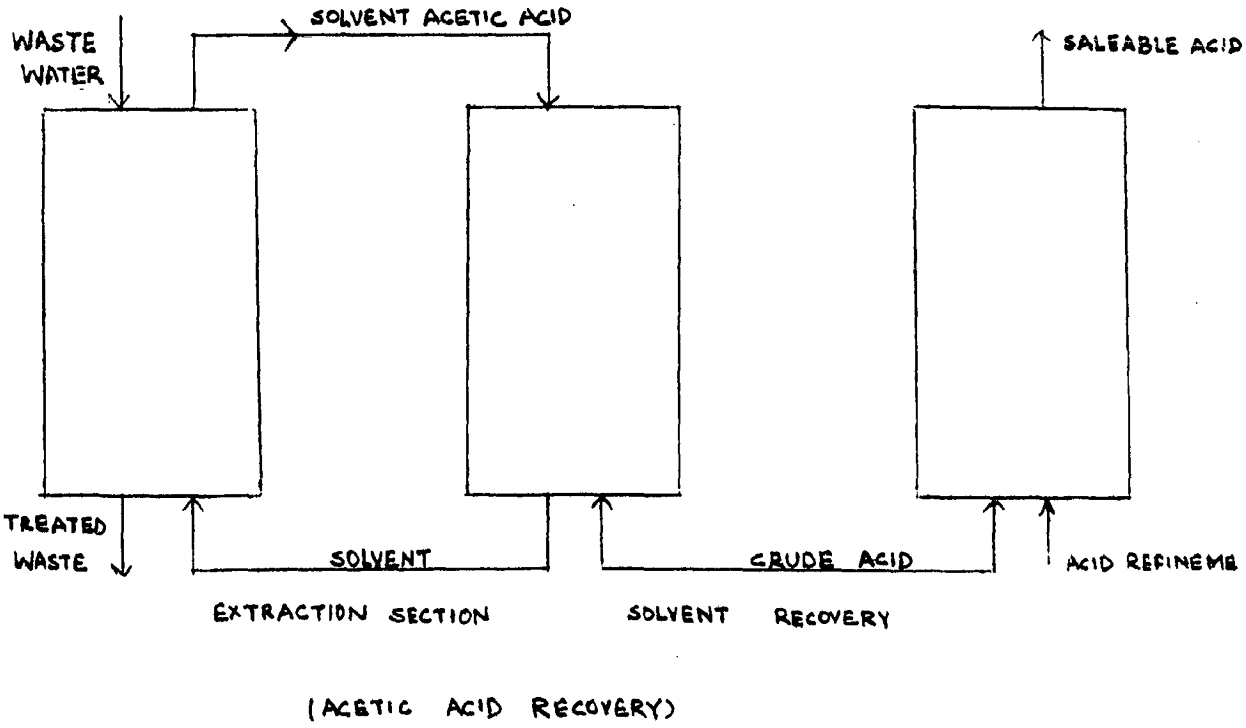
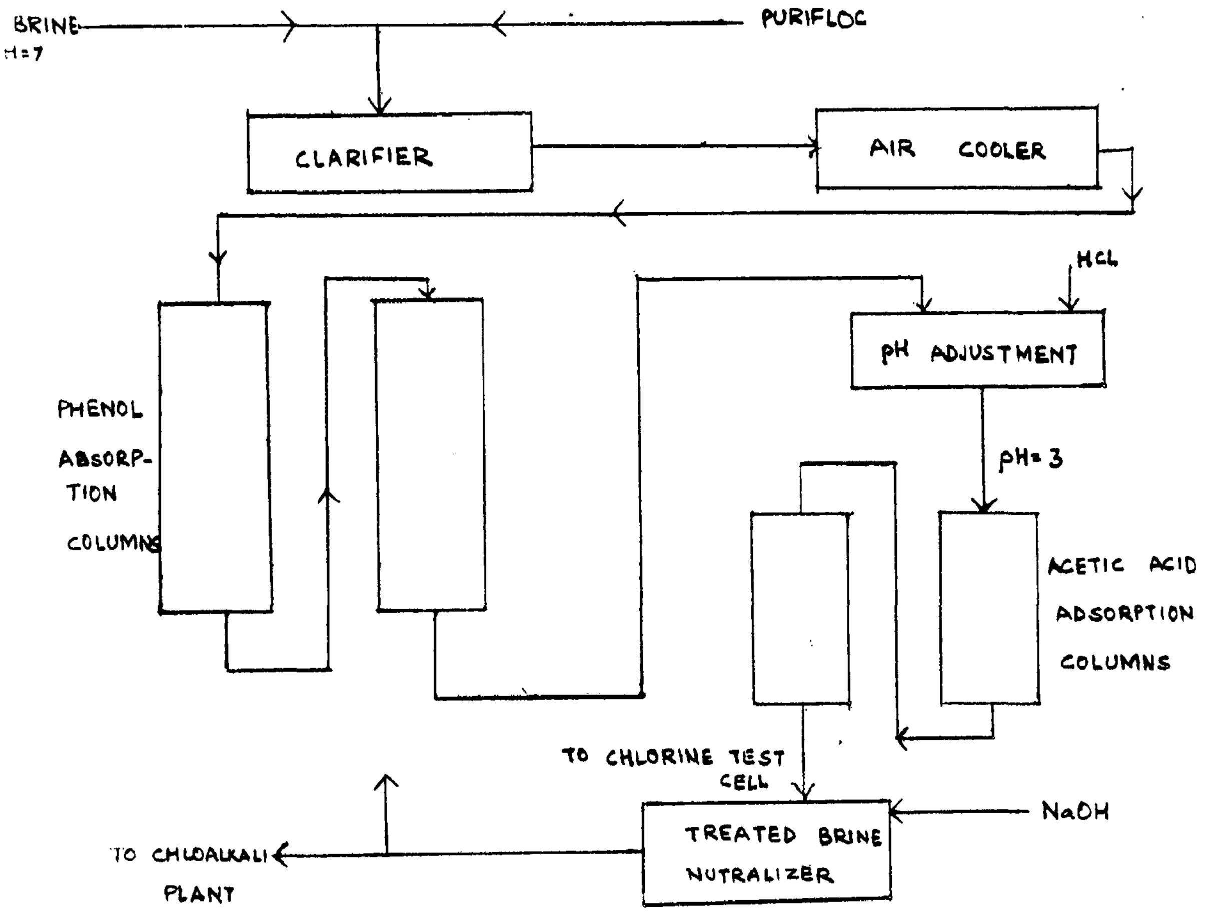
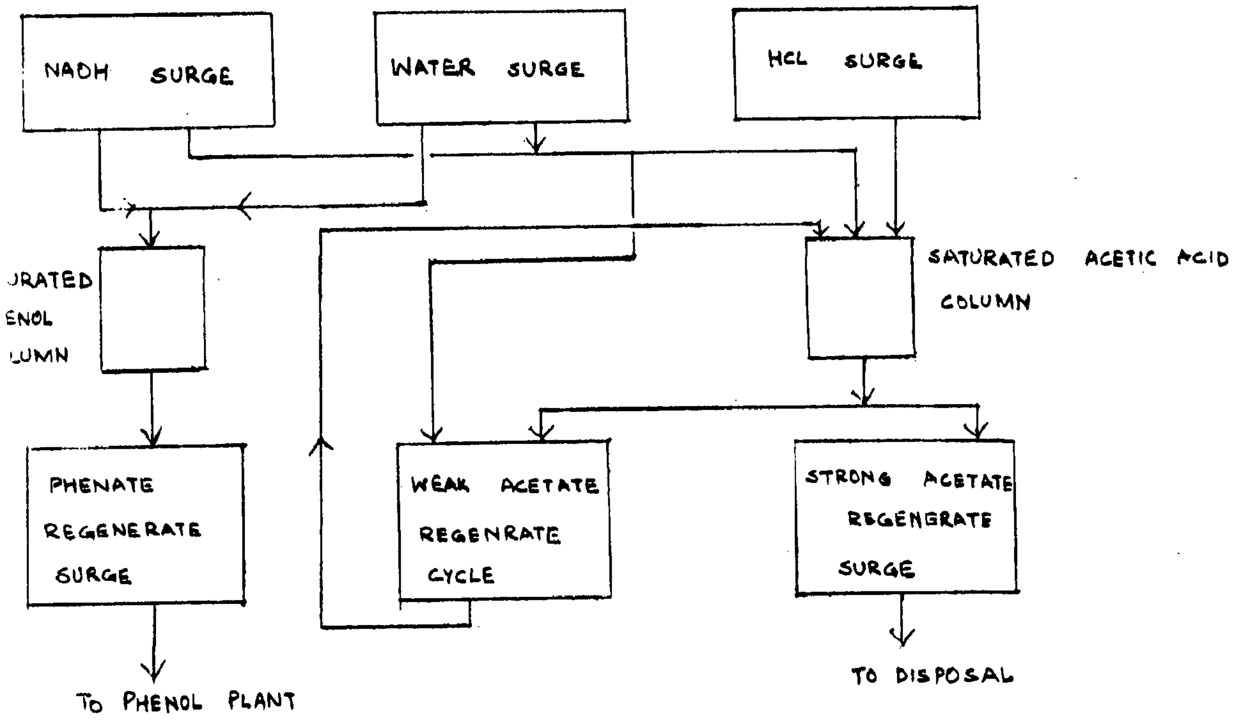


FIG 2.2 - SOLVENT EXTRACTION PROCESS



(A) SCHEMATIC DIAGRAM OF ADSORPTION



(B) SCHMETIC DIAGRAM OF REGENERATION

FIG2.3 - ADSORPTION PROCESS

CHAPTER III

EXPERIMENTAL PROCEDURE

In order to assess the performance of each adsorbent and to avoid interferenc by other elements in the waste water, the experiments were conducted with aqueuos solution of acetic acid in redistilled water.

In the present study, the adsorbent used for removal of acetic acid were

1. Activated coconut jute carbon
2. Activated bagasse carbon
3. Activated saw dust
4. Activated Rice husk

3.1 Preparation of Waste Water

Synthetic samples were prepared by dissolving acetic acid (CH_3COOH) in redistilled water at specific concentration and were used as source of acetic acid. Stock solution was prepared by dissolving 40 gm of acetic acid in 1.0 liter redistilled water to give a acetic acid concentration 40 g/l i.e. 4% solution and subsequent concentrations were obtained by diluting this solution to various desired concentration levels.

3.2 Estimation of Acid concentration

Estimation of acid concentration in waste water was done by simple titration method using standard base NaOH and phenopthelene as inidactor. The samples were titrated with standard 0.02 N NaoH to phenoptheleñe end point. Using fine tip burrete and taking care to avoid areation.

$$\text{acid concentration} = \frac{(a-b) \times N \times 6000}{\text{Ml of sample}}$$

where a = ml of NaOH used for smple

b = ml of NaOH used for blank

N = Normality of NaOH

for blank distilled water was titrated with some procedure as above

3.3 COD ESTIMATION

The COD of the samples were determined as prescribed by ISI 3025. The COD of the sample was calculated by the formula

$$\text{COD (mg/l)} = \frac{(A-B).C \times 8000}{\text{ml of sample}}$$

where

A = ml of ferrous ammonium sulphate for blank solution

B = ml of ferrous ammonium sulphate for the sample

C = Normality of the ferrous ammounium sulphate solution

3.4 EXPERIMENTAL METHOD

3.4.1 Batch Study

The adsorption kinetics equilibrium studies and the effect of different variables on the adsorption behaviour for all the adsorbent were performed in a batch system. Batch experiments are preferred in order to compare the activities of different adsorbents under identical operating conditions of these adsorption processes.

3.4.2 Procedure

100 ml of syntnetic waste of acetic acid conc (0.5% - 4%) was taken in different conical flasks. Suitable doses (.2 - 6gm / 100ml) of the adsorbent were added. The system was equilibrated by shaking thoroughly in the electric shaker. After certain time intervals the suspensions were filtered using whatman No 41 filter paper and acetic acid concentratin in filtrate analyzed by simple titration method. By this method firstly equilibration time was computed. Then optimum dose of adsorbent, effects of initial acetic acid concentration of waste water were computed.

The effects of temperature in the range of (18°- 38°C) were also studied Keeping other parameters constant. In addition to this effects of adsorbent dose on C.O.D. removal was also studied. For this initial C.O.D. of stock solution (4%) was calculated, for adsorption. batch experiments were performed as above for all the four adsorbents.

3.5 REMOVAL OF ACETIC ACID

3.5.1 Using Activated coconut Jute Carbon

Jute carbon was prepared by treating 4 parts of raw cocnut jutewith 3 parts by weight of concentrated sulphuric acid and kept in an air over maintained at 150° - 160°C for a period of 24 hours. The carbonised material was washed well with water to remove the free acid and dried at 105° - 110°C for 24 hours. The dried material was subjected to thermal activation at 800°- 850°C for a peried of 15 minutes in the absence of air. The material was ground and the particle size range (106 - 425) micron was used throughout the studies.

The variables studied on this case were equilibration time (30 - 240 min), dose (0.2 - 5gm/100ml) initial acid concentration (.5 - 4%) and temperature (18^{o}- 38^{o}C). Effect of dose (0.2 - 5 g/100ml) on COD removal was also studied. Results are given in table (3.1) through table (3.6).

3.5.2 Using Activated Bagasse Carbon

Preparation method was same as followed for activated coconut jute carbon. The variables studied in this case were adsorbent dose (0.2 - 6 g/100 ml), acid concentration (0.5 - 4%), equilibration time (30 - 210 min), temperature (18 - 38^{o}C) and for C.O.D., dose (0.2 - 6g/100ml). The results are presented in table (3.7) through table (3.12).

3.5.3 Using Activated Saw dust

Preparation method was same as followed for activated coconut jute carbon. In this case adsorbent has been taken as such the variable studied in this case were equilibration time (30 - 180 min), dose (0.2 - 4/100ml), acid concentration (0.5 - 4%) temperatur (18 - 38^{o}C) for C.O.D dose (0.2 - 4 g/100ml) and the results are presented in table (3.13) through table (3.18).

3.5.4 Using Activated Rice Husk

The preparation method was same as followed for above three adsorbent except screening of raw rice husk through screen size (600 mic.) as to remove unwanted dirt and sand. In this case also the adsorbent has been taken as such. The variable studied in this case were adsorbent dose (0.2 - 4 g/100ml), equilibration time (30 - 210 min), inital acid concentration (0.5 - 4%), tempearture (18 - 38°C) and for C.O.D., dose (0.2 - 4 g/100ml) the results are presented in table (3.19) through table (3.24).

TABLE : 3.1

Effect of Time on acetic acid removal by Activated coconut jute corbon (Adsorbent dose = 2gm/100ml, temp = 18± 1°C, Initial acid concentration 4%)

Time (Minute)	% removal	Final conc (%)
30	10.6	3.57
60	16	3.36
90	21.1	3.15
120	24.5	3.02
150	27.2	2.91
180	29.4	2.82
210	31.0	2.76
240	31.0	2.76

TABLE : 3.2

Effect of Dose on Acetic acid Removal by activated coconut jute carbon (temp = 18±1°C, initial acid concentration=4%)

Dose(gm/100ml)	% removal	Final conc (%)
0.2	14	3.44
0.4	17.85	3.286
1.0	25.25	3.11
1.5	27	2.84
2.0	31	2.76
3.0	33.5	2.66
4.0	33.5	2.66
5.0	33.5	2.66

TABLE : 3.3

Effect of Initial acid concentration on acetic acid Removal by Activated Coconut Jute Carbon)

(Temp = 18±1^{0}C, Dose = 6g/100ml)

Inital acid Conc %	% removal	Final conc (%)
0.5	26	0.37
1.0	28.1	0.719
2.0	33	1.34
3.0	33.5	1.995
4.0	33.6	2.656

Table 3.4

Effect of Temperature on Acetic acid removal by Activated Jute Carbon

(Dose = 6g/100ml, initial acid Conc = 4%)

Temp. °C	% removal	Final conc (%)
18	33.4	2.664
22	33	2.68
26	31.5	2.74
30	30.4	2.77
34	29.5	2.82
38	28.6	2.856

Table 3.5
Data for Freundlich Curve (From Table 3.2)
(Initial acid concentration = 4% , temperature = 18±1°C)

Dose, m (g)	Final Conc. ,Ce (g/l)	Amount adsorbed x, (g/l)	log(x/m)	logCe
2	34.4	5.5	0.447	1.536
4	32.86	7.14	0.252	1.516
10	29.9	10.1	0.004	1.477
15	28.4	11.8	- 0.104	1.45
20	27.6	12.4	- 0.208	1.44
30	26.6	13.4	- 0.35	1.425

TABLE : 3.6
Effect of Activated coconut Jute carbon Dose on C.O.D Removal

(Initial C.O.D.=40,500 mg/l, temp=18±1°C)

Dose (g/100ml)	C..O.D. remain (mg/l)	% C.O.D.removal (%)
0.2	35,000	13.58
0.4	33,500	17.28
1	31,000	23.45
1.5	29,000	28.39
2	28,000	29.6
3	27,000	32.09
4	27,000	33.33
5	27,000	33.33

TABLE : 3.7

Effect of time on acetic acid removal by Activated Bagasse Carbon

(Adsorbent dose - 2gm/100ml, temp = 18±1°C Initial acid Concntration =4%)

Time (minute)	% removal	Final conc (%)
30	13.0	3.48
60	16.0	3.36
90	24.9	3.0
120	34.3	2.63
150	42.5	2.3
180	46.0	2.16
210	46.0	2.16

TABLE : 3.8

Effect of Activated Bagasse Carbon Dose on Acetic acid removal

(temp = 18±1°C, initial acid conc=4%)

Dose(gm/100ml)	% removal	Final conc (%)
0.2	23.5	3.06
0.4	37.6	2.66
1.0	41.5	2.34
1.5	43.6	2.26
2.0	46.4	2.16
3.0	48	2.08
4.0	49.5	2.02
5.0	51	1.96
6.0	51.2	1.95
7.0	51.2	1.95

TABLE : 3.9
Effect of Inital acid concentration on Acetic acid Removal by Activated Bagasse Carbon
(Dose = 6g/100ml Temp = 18±1°C)

Initial acid Conc %	% removal	Final conc (%)
0.5	45	0.275
1.0	46	0.54
2.0	47.1	1.06
3.0	48.9	1.533
4.0	51.1	1.957

TABLE 3.10
Effect of Temperature on Acetic acid Removal by Activated Bagasse Carbon
(Dose = 6g/100ml. Inital acid Conc = 4%)

Temp. °C	% removal	Final conc (%)
18	51.2	1.952
22	49	2.04
26	46.5	2.14
30	44.4	2.224
34	42	2.32
38	39.6	2.416

Table 3.11
Data for Freundlich Curve (From Table 3.8)
(Initial acid concentration = 4% , temperature = 18±1°C)

Dose, m (g)	Final Conc. , Ce (g/l)	Amount adsorbed x, (g/l)	log(x/m)	logCe
2	30.6	9.4	0.672	1.486
4	26.56	13.49	0.429	1.424
10	23.4	16.6	0.22	1.377
15	22.56	17.4	0.064	1.353
20	21.6	18.4	-0.036	1.334
30	20.8	19.2	-0.194	1.318
40	20.2	19.8	-.0305	1.305
50	19.6	20.4	-0.389	1.292

TABLE : 3.12
Effect of Activated Bagasse Dose on C.O.D. Removal

(Initial C.O.D.=40,500 mg/l, temp=18±1°C)

Dose (g/100ml)	C..O.D. remain (mg/l)	% C.O.D.removal (%)
0.2	31,500	22.2
0.4	26,000	35.0
1	24,000	40.7
1.5	23,000	43.2
2	22,000	45.67
3	21,500	46.9
4	21,000	48.1
5	20,000	50.61
6	20,000	50.61

TABLE : 3.13

Effect of Time on acetic acid removal by Activated Sawdust

(Adsorbent dose = 1 gm/100ml, Temp = 18±1^{0}C, Initial acid Concentration = 4 %)

Time (minute)	% removal	Final conc (%)
30	9.5	3.62
60	15	3.4
90	16.3	3.35
120	17.5	3.3
150	18.5	3.26
180	18.5	3.26

TABLE 3.14

Effect of Activated Saw dust dose on Acetic acid Removal
(Temp -18± 1^{0}C Initial acid Conc = 4%)

Dose (g/100ml)	% removal	Final conc (%)
0.2	6.65	3.74
0.4	10.5	3.58
1.0	18.5	3.26
1.5	22.5	3.10
2.0	25.5	2.98
3.0	25.6	2.98
4.0	25.61	2.98

Table 3.15
Effect of Initial acid concentration on Acetic acid Removal by Activated Saw Dust
(Temp = 18±1°C , Dose = 6g/100ml)

Initial acid Conc %	% removal	Final conc (%)
0.5	16.5	0.4175
1.0	17.4	0.826
2.0	18.5	1.63
3.0	23.6	2.242
4.0	25.6	2.976

Table 3.16
Effect of temperature on acetic acid removal by Activated saw Dust
(dose - 6 g/100ml, initial acid concentraion 4%)

Temperature °C	% removal	Final concentration (%)
18	25.6	2.97
22	25	3
26	24.5	3.02
30	24.1	3.056
34	23.1	3.08
38	22.5	3.1

Table 3.17
Data for Freundlich Curve (From Table 3.14)
(Initial acid concentration = 4% , temperature = 18±1°C)

Dose, m (g)	Final Conc. , Ce (g/l)	Amount adsorbed x, (g/l)	log(x/m)	logCe
2	37.4	2.66	0.124	1.572
4	35.8	4.2	0.211	1.559
10	32.6	7.9	0.130	1.513
15	31	9	0.221	1.491
20	29.8	10.2	-0.292	1.474

TABLE 3.18
Effect of Activted Saw Dust dose on C.O.D. Removal
(Initial C.O.D.=40,500 mg/l, temp=18±1°C)

Dose (g/100ml)	C.O.D. remain (mg/l)	% C.O.D. removal
0.2	38,000	6.17
0.4	36,500	9.87
1	33,500	17.28
1.5	31,500	22.22
2	30,500	24.69
3	30,500	24.69
4	30,500	24.69

TABLE 3.19

Effect of Time on Acetic Acid removal by Activated Rice husk (adsorbent dose = 2 g/100ml, Temp = 18±1°C, Initial acid Conc = 4%

Time (minute)	% removal	Final conc (%)
30	2	3.92
60	4.6	3.82
90	8.7	3.65
120	11	3.56
150	12.5	3.5
180	13.6	3.46
210	13.6	3.46

TABLE : 3.20

Effect of Activated Rice husk Dose on Acetic acid Removal (Temp = 18±1°C, Initial acid concentration = 4%)

Dose (g/100ml)	% removal	Final conc (%)
0.2	5	3.8
0.4	7.8	3.69
1.0	11	3.56
1.5	12.5	3.5
2.0	13.7	3.45
3.0	13.7	3.45
4.0	13.8	3.45

TABLE : 3.21
Effect of Initial acid concentration on Acetic acid Removal by Activated Rice husk

(Temp = 18±1°C, Dose = 6g/100ml)

Initial acid Conc %	% removal	Final conc (%)
0.5	14.4	0.428
1.0	15.5	0.845
2.0	16.1	1.368
3.0	15	2.55
4.0	13.8	3.448

Table 3.22
Effect of temperature on acetic acid removal by Activated Rice husk
(dose - 6 g/100ml , initial acid concentration 4 %)

Temperature °C	% removal	Final concentration (%)
18	13.8	3.458
22	13.6	3.46
26	13	3.48
30	12.8	3.488
34	12.4	3.504
38	11.9	3.524

Table 3.23
Data for Freundlich Curve (From Table 3.20)
(Initial acid concentration = 4% , temperature = 18±1°C)

Dose, m (g)	Final Conc. , Ce (g/l)	Amount adsorbed x, (g/l)	log(x/m)	logCe
2	38	2	0	1.58
4	36.9	3.1	- 0.119	1.567
10	35.6	4.4	- 0.356	1.551
15	35	5	- 0.477	1.544
20	34.2	5.48	- 0.562	1.538

TABLE : 3.24
Effect of Activated Rice husk dose on C.O.D. Removal

(Initial C.O.D.=40,500 mg/l, temp=18±1°C)

Dose (g/100ml)	C.O.D. remain (mg/l)	% C.O.D.removal
0.2	39,000	3.7
0.4	37,000	7.4
1	36,500	9.87
1.5	36,000	11.1
2	35,500	12.34
3	35,000	13.58
4	35,000	13.58

Table 3.25
CHARACTERISTICS OF ADSORBENTS

Adsorbments	Moisture %	V.m %	Ash %	Combustible material %	Si %	Ca %	Al_2O_3 %
Activated Coconut Jute Carbon	7.5	17.18	24.33	75.67	18.21	3.28	2.86
Activated Bagasse Carbon	11.39	20.66	5.44	94.56	3.83	1.26	1.35
Activated Saw Dust	11.47	23.74	11.45	88.55	5.43	4.15	1.87
Activated Rice Husk	10.68	19.46	27.56	72.44	20.46	4.25	2.85

Table 3.26 Freundlich Constants

ADSORBENTS	$\frac{1}{n}$	K
Activated bagasse carbon	6.97	4.78×10^{-10}
Activated coconut jute carbon	7.1	3.65×10^{-11}
Activated saw dust	4.35	2.14×10^{-7}
activated rice husk	14.3	2.09×10^{-23}

CHAPTER IV

RESULTS & DISCUSSION

Four different adsorbents namely activated coconut jute carbon, activated bagasse carbon, activated saw dust and activated rice husk were studied for the removal of acetic acid from an aqueous solution.

The important parameters having profound effect on the rate of adsorption are nature of adsorbent and adsorbate, initial acetic acid concentration, contact time and temperature. Batch studies were carried out to observe the effects of these parameters on the adsorption of acetic acid. Effect of adsorbent dose on COD removal was also observed.

4.1 REMOVAL OF ACETIC ACID BY ACTIVATED COCONUT JUTE CARBON :

4.1.1 Effect of Activated Coconut Jute Dose

Fig (4.2) shows the effect of activated cocount jute dose on the acetic acid removal from the aqueous solution containing 4 % (40gm/l) acetic acid.

It was observed that at room temp (18± 1°C), 33.5% acetic acid could be removed when treated with 3 gm of activated coconut jute in 100 ml solution. At adsorbent dose greater than this, acetic acid removal was not increased, which indicated that 3 g/100ml activated jute carbon is an optimum dose for the removal of acetic acid under these conditions. Figure (4.6) shows the effect of activated coconut jute corbon dose or the percent C.O.D. removal from the waste containing 4% acetic acid (pH = 2.45) at temperature 18±1°C. A dose of 30 g/l was found to be an optimum dose, since any further increase in activated bagasse carbon dose did not substantially increase the percentage removal of acetic acid.

The adsorption data at different carbon dose is fitted to linearised Freundalich isotherm which is of the form (see fig 4.5).

$$\text{Log}\ \frac{x}{m} = \log k + \frac{1}{n} \log Ce$$

Where, $\frac{x}{m}$ is the amount of acetic acid adsorbed per unit of adsorbent in gm/gm, Ce, is equilibrium conc. of substrate, K is a constant (Which is a measure of adsorption capacity) and $\frac{1}{n}$ is another constant, measure of adsorption intensity). The plot revealed the values of the constants as

$$k = 3.65 \times 10^{-11}$$

$$\frac{1}{n} - 7.1$$

4.1.2 Effect of Initial Acetic Acid Concentration

Figure (4.3) shows the percentage removal of acetic acid as a function of increased intial concentration of acetic acid. The activatd coconut jute carbon dose was fixed at 60 g/l. It may observed that around 33.5% removal of acetic acid is achieved at 3% initial concantration (pH = 2.52) where as at lower concentrations of 2% (pH=2.6), 1% (pH=2.7), 0.5% (pH=2.89) of actic acid, the corrospsponding values were 33%, 28% and 26% repectively.

4.1.3. Effect of Temperature

Fig (4.4) shows the effect of temperature on percent acetic acid removal from the synthetic water containg 4% acetic aid. It may be observed from the graph that the increase in temperature leads to linear decrease in the percent acetic acid removal. A reduction from 33.4% to 28.6% of acetic acid removal was observed when the temperature was increased form 18°C to 38°C.

4.2 REMOVAL OF ACETIC ACID BY ACTIVATED BAGASSE CARBON

4.2.1 Effect of Adsorbent Dose

Fig (4.8) shows the effect of activated bagasse carbon dose on the percent acetic acid removal from the waste containing 4% acetic acid (pH=2.45) at temperature 18±1°C. It can be seen that, as the dose increase, percent acetic acid removal increases. A dose of 50 g/l was found to be an optimum dose, since any further increase in activated bagasse dose did not substantially increase the percentage removal of acetic acid. Fig (4.12) shows the effect of adsorbent on percent C.O.D. removal from the waste containng 4% acetic acid. The plot indicates that at room temperature (18±1°C) 50.6% COD is removed when treated with 5 gm activated bagasse carbon dose in 100 ml solution.

The adsorption data at diffrent carbon dose was fitted to linearised freundlich adsorption isotherms, which is of the form (see fig 4.11).

$$\text{Log}\,\frac{x}{m} = \log K + \frac{1}{n}\log Ce$$

$\frac{x}{m}$, Ce, K, and ($\frac{1}{n}$) have same meanings as 4.1.1

The plot revealed the values of the constants as

$$K = 4.78 \times 10^{-10}$$

$$\frac{1}{n} = 6.97$$

4.2.2 Effect of Initial Acetic Acid Concentration

Fig (4.9) shows the percentage removal of acetic acid as a function of its increased initial concentration at temperature 18±1°C and fixed adsorbent dose of 60 g/l. The plot shows that as the initial acid concertration increases, the percentage acetic acid removal increases at the initial acid concentration of 4% (pH=2.45) a 51.1% acid removal was observed, where as at 3% (pH=2.52), 2% (pH=2.60), 1% (pH=2.7) and .05 % (pH=2.89) initial acid concentration, the percent removal was 48.9%, 47%, 46% and 45% respectively.

4.2.3 Effect of Temperature

Fig (4.10) show the effect of temperature on percent acetic acid removal from the feed containing 4% acetic acid. It may be observed from the graph that as the temperature increases, percent removal of acid decreases. A reduction from 51.2% to 39.6% was observed when the temperature was increased from 18°C to 38°C.

4.3 REMOVAL OF ACETIC ACID BY ACTIVATED SAW DUST

4.3.1 Effect of Adsorbent Dose

Fig (4.14) represents the effect of activated saw dust dose on the percent acetiv acid removal from the aqueous feed containing 4 % acetic acid. Fig (4.14) shows that at room temperature (18±1°C), 25.5% acid was removed when treated with. 3g activated saw dust dose. In 100 ml solution. Beyond this dose increase in the percent acetic acid removal was very small.

Fig (4.18) shows the effect of activated saw dust dose on the percent C.O.D.acid removal from the feed containing 4% acetic acid. Fig (4.18) follows the trends of fig (4.14) at above conditions and 2g saw dust in 100 ml solution was found to be optimum which reported 24% removal of C.O.D.

The adsorption data at different activated saw dust dose was fitted to linearised Freundlich adsorption isotherm, which is of the form (see fig 4.17)

$$\text{Log}\ \frac{x}{m} = \log K + \frac{1}{n} \log Ce$$

$\frac{x}{m}$, Ce, K and $(\frac{1}{n})$ have same meaning as in 4.2.1.

The plot revealed the values of the freundlich constants

$$K = 2.19 \times 10^{-7}$$

$$\frac{1}{n} = 4.35$$

4.3.2 Effect of Initial Acetic Acid Concentration

Fig (4.15) depicts the percentage removal of acetic acids as a function of its increased initial concentrations at temperature (18±1°C).

The plot shows that as the initial acid concentration increases, the percentage cetic acid removal increases . At the intial acid concentration of 4 % (pH=2.45) a 25.6% removal was observed whereas at acid concentrations of 3% (pH=2..52), 2% (pH=2.6) 1% (pH=2.7) and 0.5% (pH=2.89) removals of the order of 23.6%, 18.5%, 17.4% and 165% respectively were observed.

4.3.3 Effect of Temperature

Fig (4.16) shows the effect of temperature on percent acetic acid removal from the synthetic feed containing 4% acetic acid. It may be observed from the graph that the increase in temperature leads to a linear decrease in the percent acetic acid removal. A reduction from 25.6% to 22.5% of acetic acid removal was observed when the temperature was incereased from 18°C to 38°C.

4.4 REMOVAL OF ACETIC ACID BY ACTIVATED RICE HUSK

4.4.1 Effect of Adsorbent Dose

Fig (4.10) shows the effect of activated rice husk dose on the percent acetic acid removal from the feed containing 4 % acetic acid at room temperature (18±1°C). As the dose increases percent acetic acid removal increases. A maximum removal of around 13.7% was observed with 20 g/l of adsorbent dose, which did not increase further at still higher dose.

Fig (4.24) shows the effect of adsorbent dose on the C.O.D. removal, which follows the above trend.

The adsorption data at different adsorbent dose was fitted to linearised Freundlich adsorption isotherm (fig 4.23).

The plot revealed the values as

$K = 2.09 \times 10^{-23}$

$\frac{1}{n} = 14.3$

4.4.2 Effect of Initial acid Concentration

percentage removal of acetic acid as a function of the increased initial concentration at temperature (18±1°C) has been shown in fig 4.21. The plot shows that percentage removal of acetic acid increases as the concentration increases from 0.5 to 2% , then it starts decreasing with further increase in initial acid concentration.

At the initial acetic conc of 0.5% (pH=2.89) a 14.4 % acetic acid removal was observed where as at 1% (pH=2.7%), 2% (pH=2.6) and 3% (pH=2.52) the percent removal were 15.5%, 16.1%, and 15% respectively. At the highest initial concentration of 4%, only 13.8% removal took place.

4.4.3 Effect of Temperature

Fig (4.22) shows the effect of temperature on percent acetic acid removal from the synthetic waste containing 4% acetic acid. It may be observed that with the increases in temperature percent acetic acid removal decreases linearly. A reducton from 13.8% to 11.9% of acetic acid was observed when the temperature was increased from 18° to $38^{\circ}C$.

4.5 COMPARATIVE STUDY OF ALL THE FOUR ADSORBENTS

4.5.1 Effect of Dose

The comparative study has been shown in fig (4.25). The results indicate that out of the four adsorbents studied, activated bagasse carbon give the maximum removal at all the levels of the adsorbent dose, followed by activated coconut jute carbon and activated saw dust. The activated rice husk was found to be the poorest of all. How ever, the rate of increase in the percent removal was of the similar nature, i.e., in all the cases an optimum dose was obtained beyond which there was no appreciable increase in the percent removal.

4.5.2 Effect of Temperature

Fig (4.26) depicts the effect of temperature on the behaviour of all the adsorbents. The results, indicate that among the four adsorbent studied, activated bagasse carbon gave the maximum removal of acetic acid at all temperature levels followed by activated coconut jute carbon, activated saw dust and activated rice husk. There has been about 22% drop in the percent removal value by activated bagasse carbon at temperature 38^{o}C with respect to its value at temperature 18^{o}C, which in case of activated coconut jute carbon, activated saw dust and activated rice husk it was about 14.4%, 12% and 13% respectively for the same range of temperature drop.

4.5.3 Effect of Initial Acid concentration

The comparative study has been shown in fig (4.27). The results indicate that out of the four adsorbent studeid, activated bagasse carbon gave the maximum removal at all the lavel of the initial acid concentration followed by activated coconut jute carbon, activated saw dust and activated rice husk. Activated bagasse carbon, activated jute carbon, activated sawdust gave maximum removals of 51.1 %, 33 % and 25.6% respectively at 4% initial concentration, where as activated rice husk gave the maximum removal of 16.1% at initial acetic acid concentration of 2%.

4.6 DISCUSSION

4.6.1 Effect of adsorbent dose

Results, in general, have revealed the increase in the percent removal with adsorbent dose upto a certain lavel and beyond that a more orless constant rate of removal was observed. This phenomena may be explained as due to the increase in adsorbent dose more and more adsorbed surface is available for the solutes to adsorb and this increase the percentage adsorption. However, the very slow increase, if any beyond the optimum adsorbent dose may be attributed to the attainment of equilibrium between the adsorbate and adsorbent at the existing operating conditions, rendering adsorbent incapable of further adsorption.

4.6.2 Effect of Temperature

The temperature dependence of adsorption process is of a very complex in nature. Thermodynamic parameters like heat of adsorption and the energy of activation play an important role in predicting the adsorption behaviour & both are strongly temperature dependent. Heat of adsorption influence the equilibrium adsorption capacity and also indicate that the nature of interaction taking place between the adsorbate & adsorbent rate of adsorption is dependent on the energy of activation.

It has been generally observed that with the increase in temperature the percent removal due to the adsorption decreases, which is also evident from our experimental studies. This phenomena can also be explained on the basis of the fact that at higher temperature, due to high intrinsic energy of the adsrobing molecules, the probability of adhering to the adsorbent surface are less. Also the overall effect of the temperature is due to its effect on acetic acid , adsorbent bond, the water adsorbent bond, the acetic acid - acetic acid interactions and the water acetic acid interactions. The water - adsorbent is important because adsorption of acetic acid probably involves displacement of water molecules from the adsorbent surface. It may be concluded that at higher temperature, the decrease in the adsorption could be due to the weakening of either of these bonds or due to the possible exothermic nature of the adsorption process.

4.6.3 Effect of Initial concentration

The general trend of the plots show that % acetic acid removal more or less, increases with the acetic acid concentration in the feed. The plots in general also indicate. that the adsorbent which were based on cheap agricultural sources, had poor adsortion capacity for the acetic acid. The increase in the adsorption with initial feed concentration may be attributed to the fact that the adsorbents having poor affinity towards the adsorbent have lower capacity for the adsortion at low acid concentration (at the prevailing experimental conditions). As the concentration of acid in the feed increases, the probability of acetic acid molecular to reach to the adsorbent surfaces increases which assure increse in the adsorption rate.

Fig (4.28) shows the freundlich isotherm of all the adsorbent. The values of the freundlich constants K and $\frac{1}{n}$ are give table 3.26. It may be observed that in general the values of $\frac{1}{n}$ are greater than 1.0, it threfore, suggests that the adsorbents studied in the present case are not very good for the adsorption of acetic acid molecules. However a maximum conversion of around 5.2% may be obtained with activated bagasse corbon for the inital acid concentration of 4% at $18\pm1^{o}C$ with an adsorbent dose of 5 g/100ml. The applicability of these adsorbent may be commercial if they are used in multiple contact. The lower activity may thus be compensated with the lower cost.

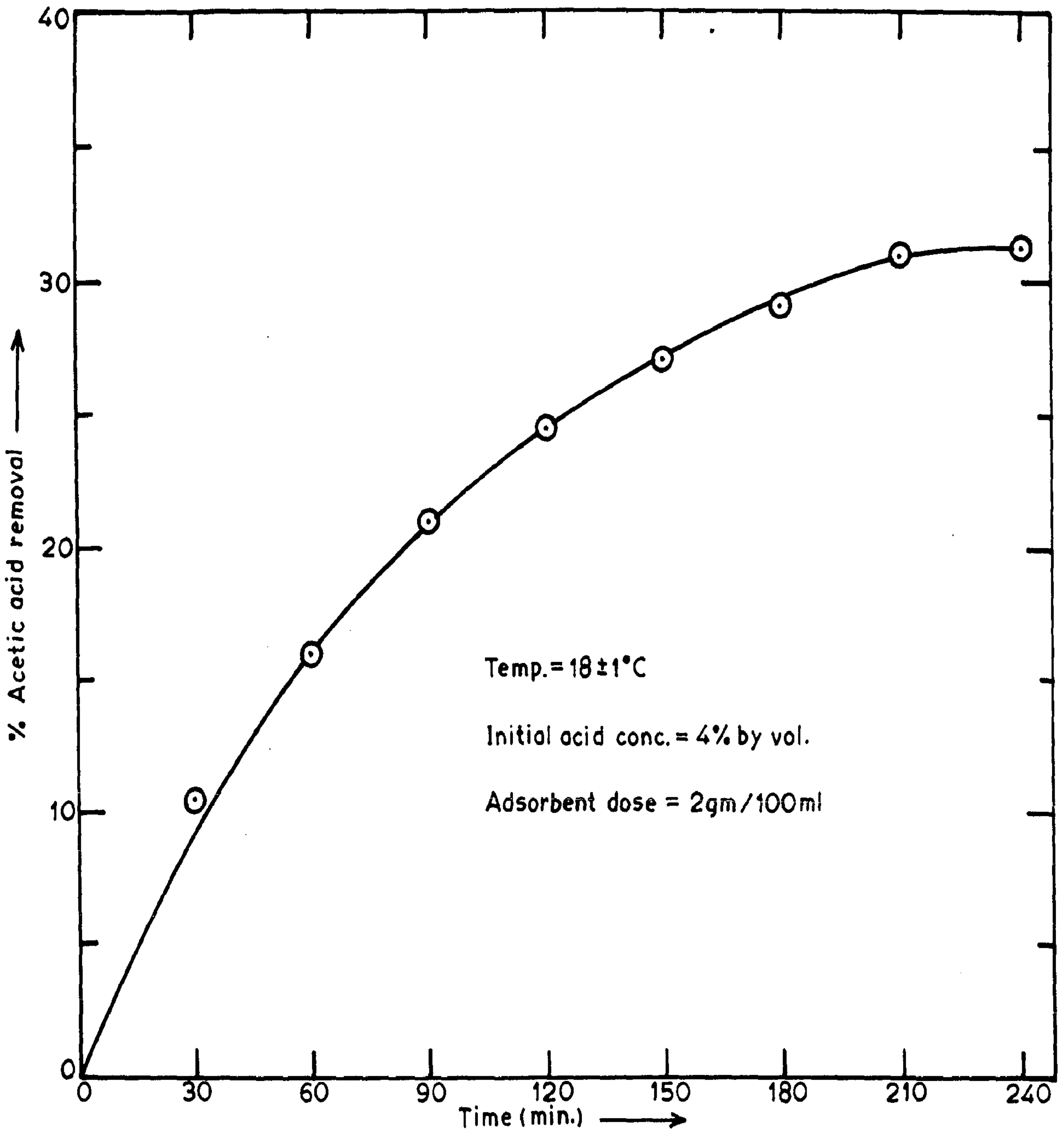


Fig. 4.1 . Equilibration time curve for activated jute carbon.

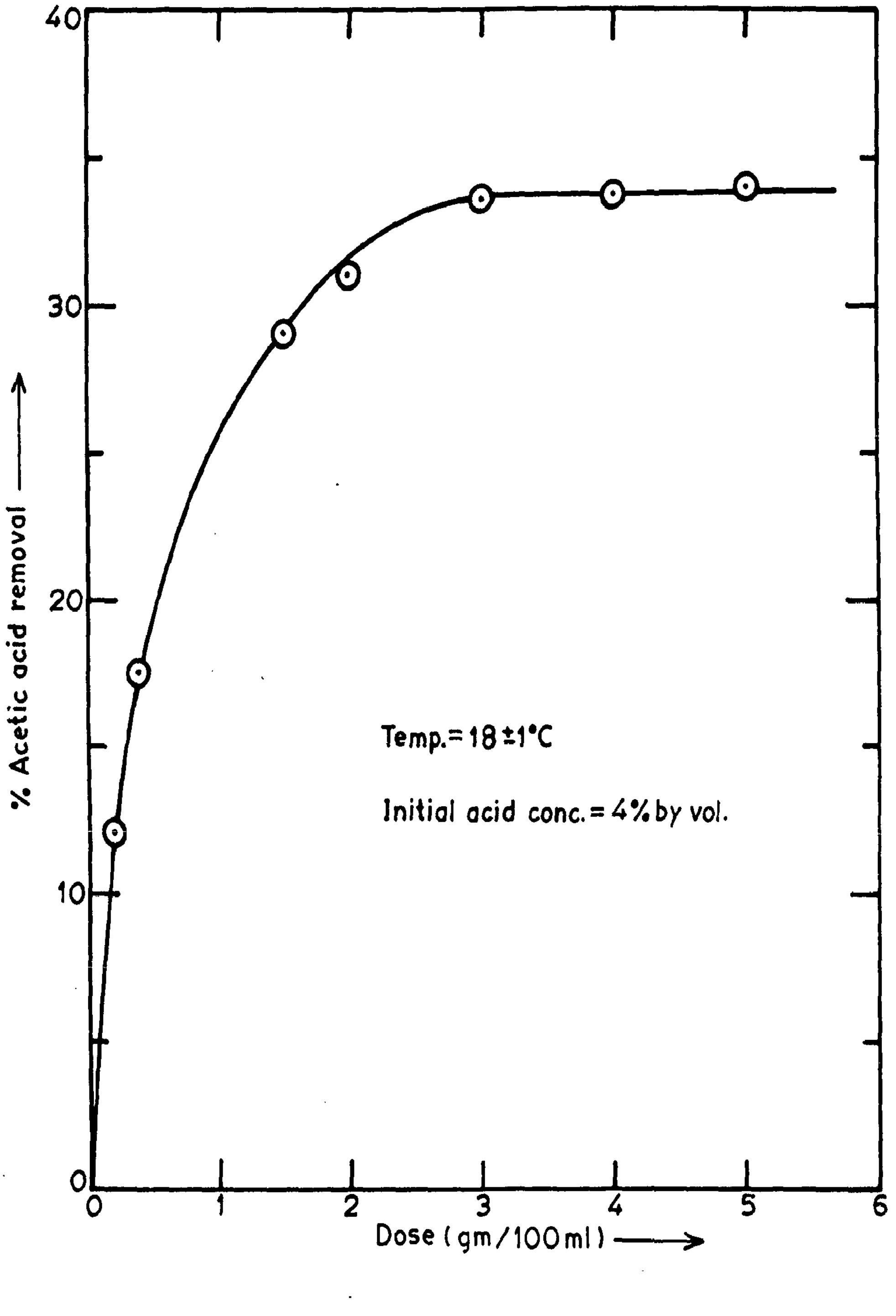


Fig.4. 2 Effect of adsorbent dose (activated jute carbon).

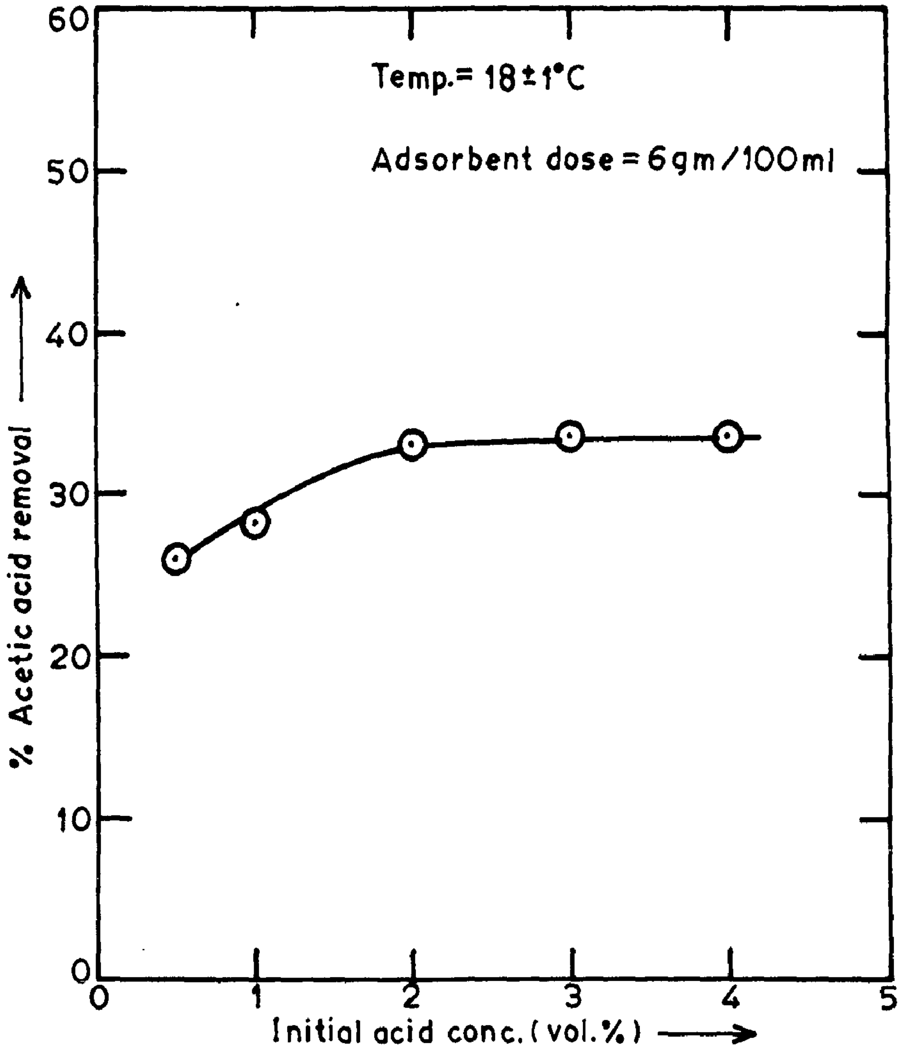


Fig.4.3. Effect of initial acid conc. (activated jute carbon).

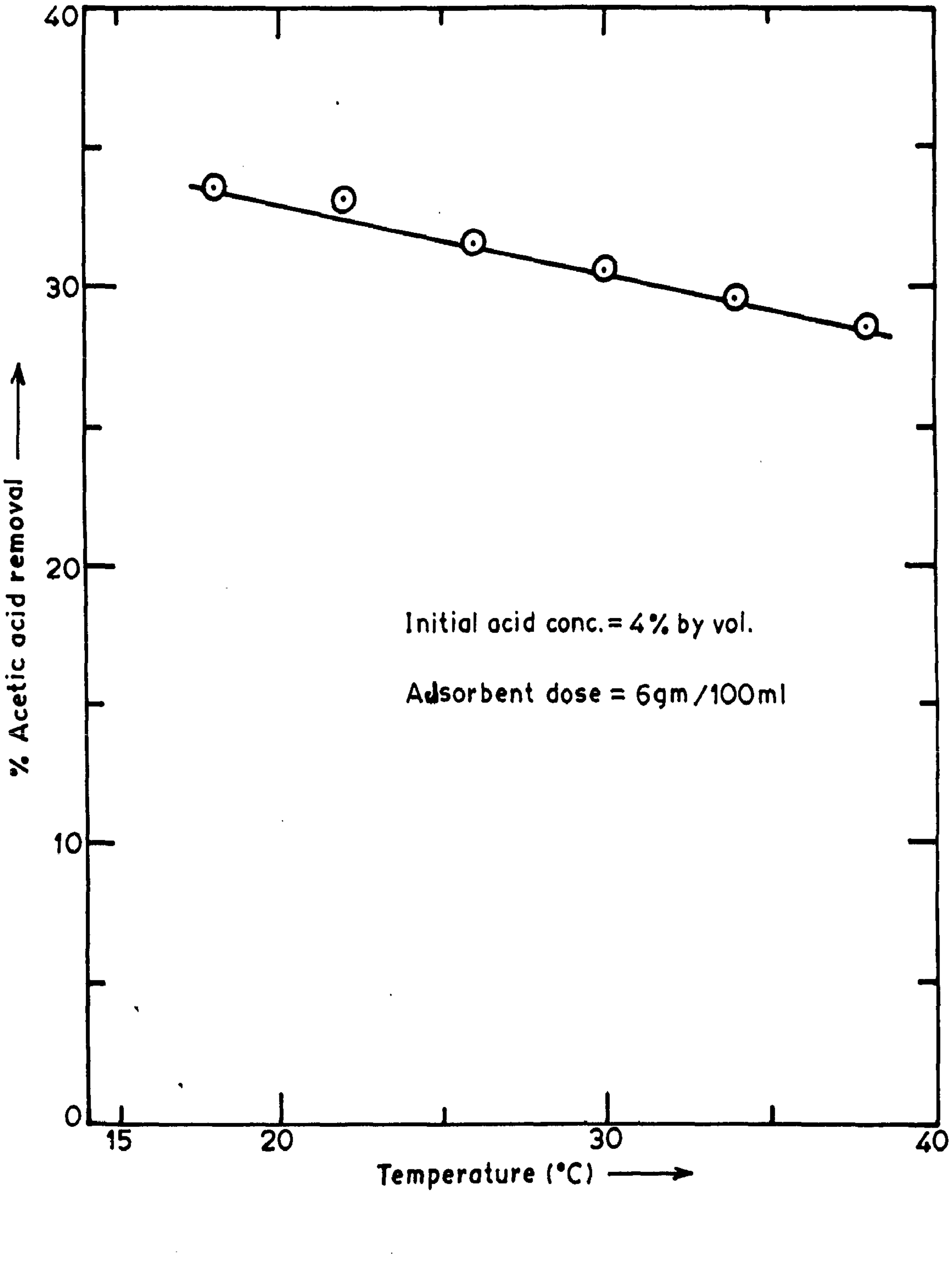


Fig.4.4 . Effect of temperature (activated jute carbon).

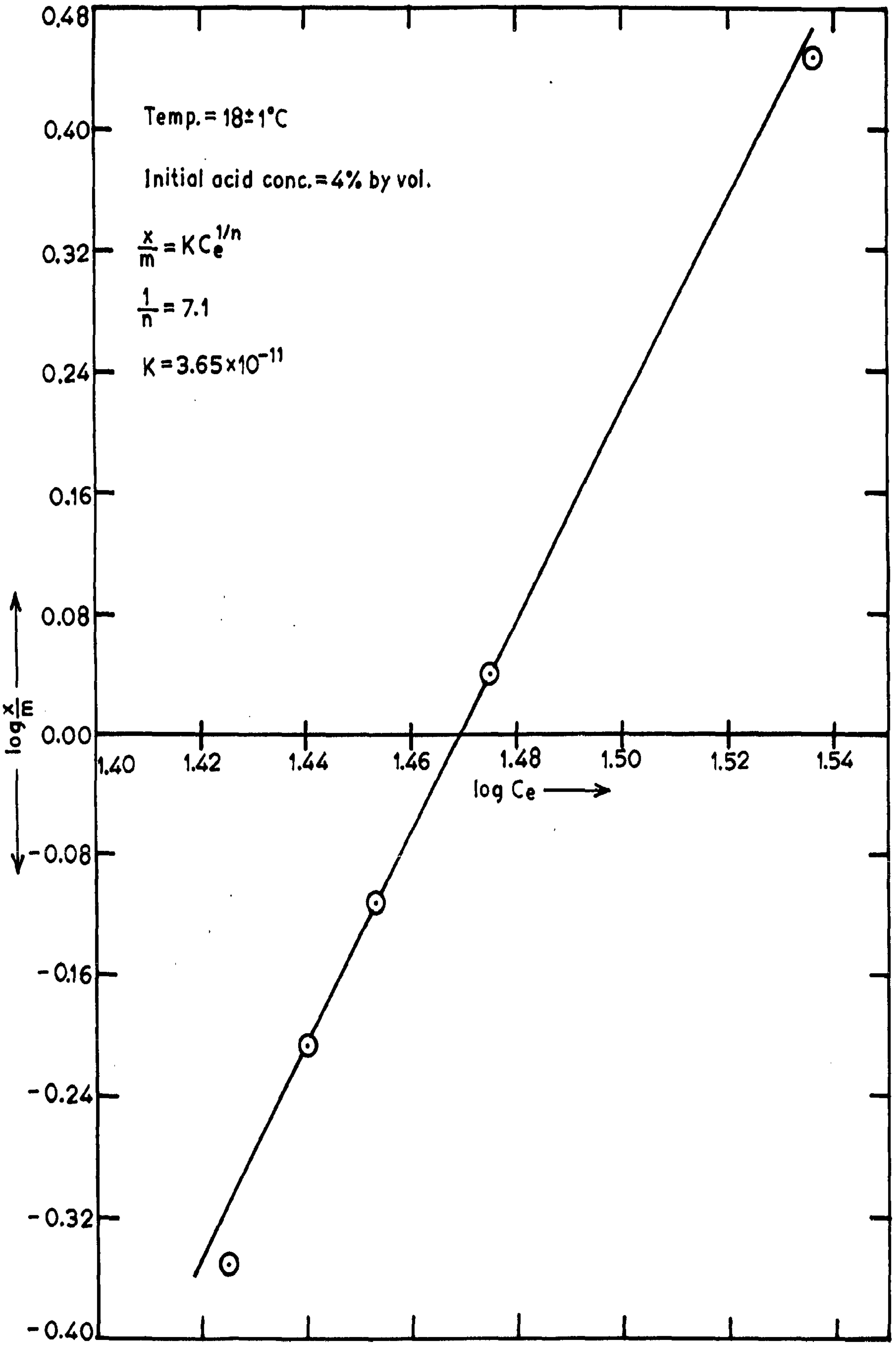


Fig.4.5. Freundlich isotherm (active coconut jute carbon).

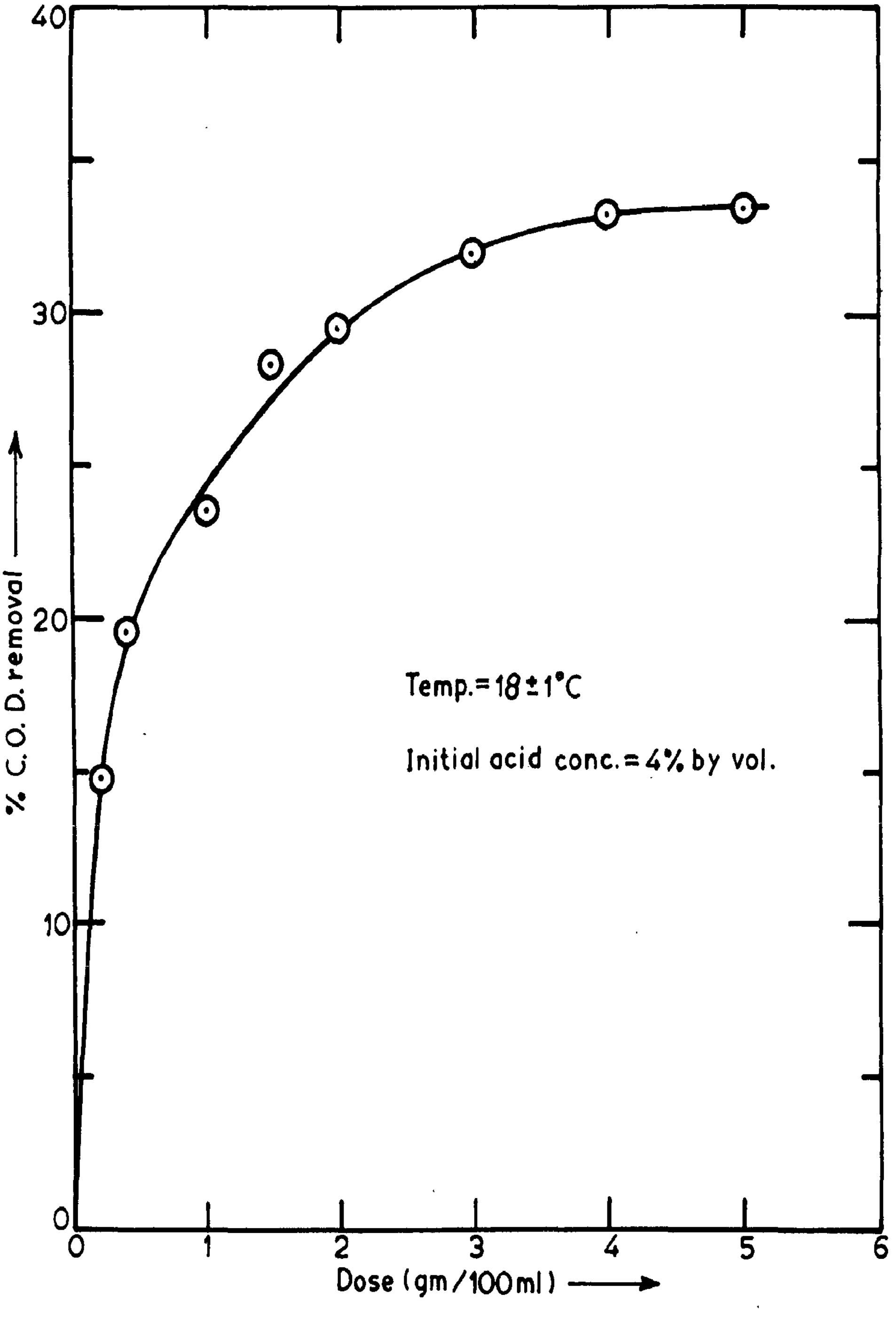


Fig.4.6 . Effect of dose on % removal of C.O.D. (activated jute carbon).

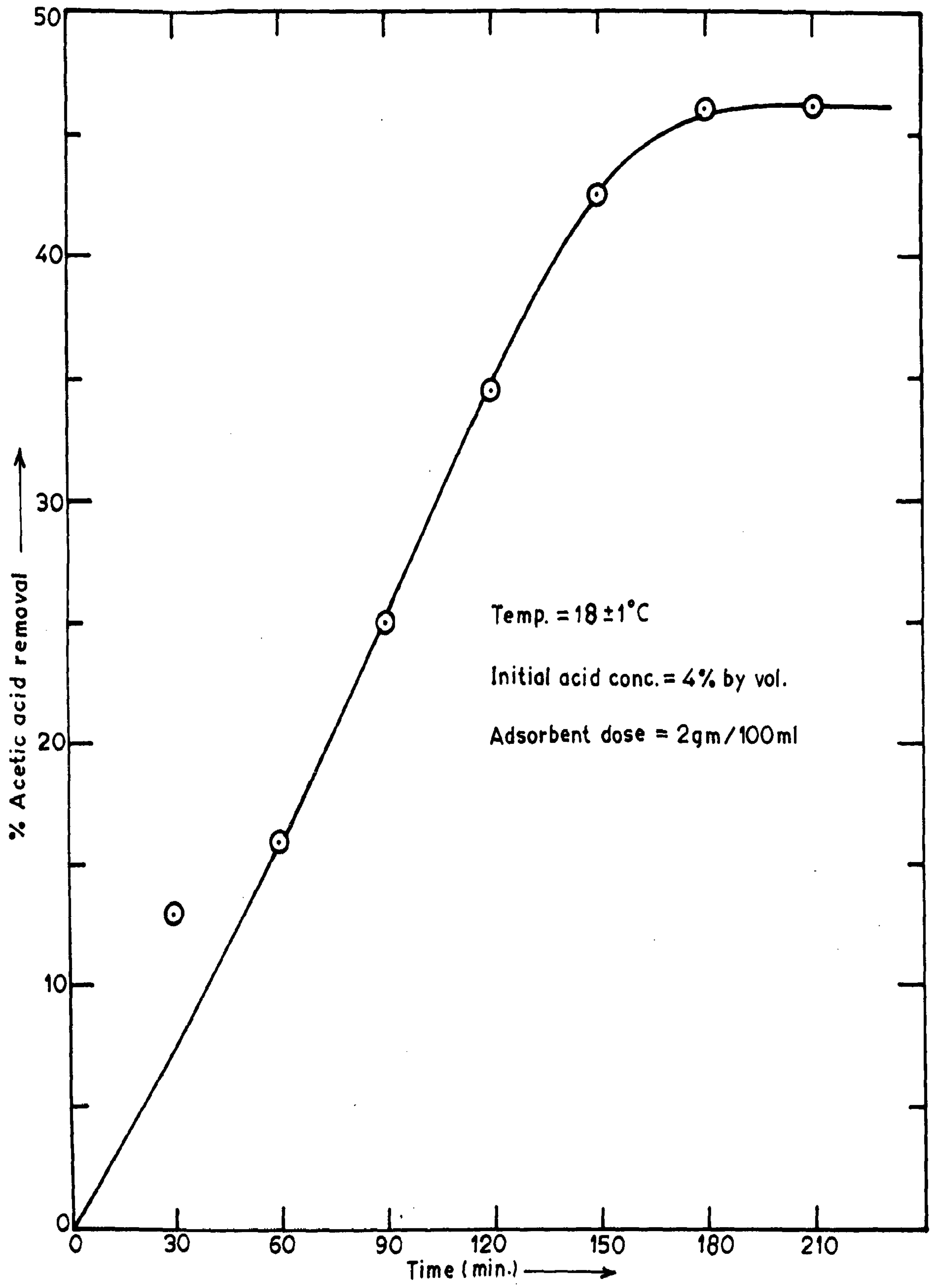


Fig. 4.7. Equilibration time curve for activated bagasse carbon.

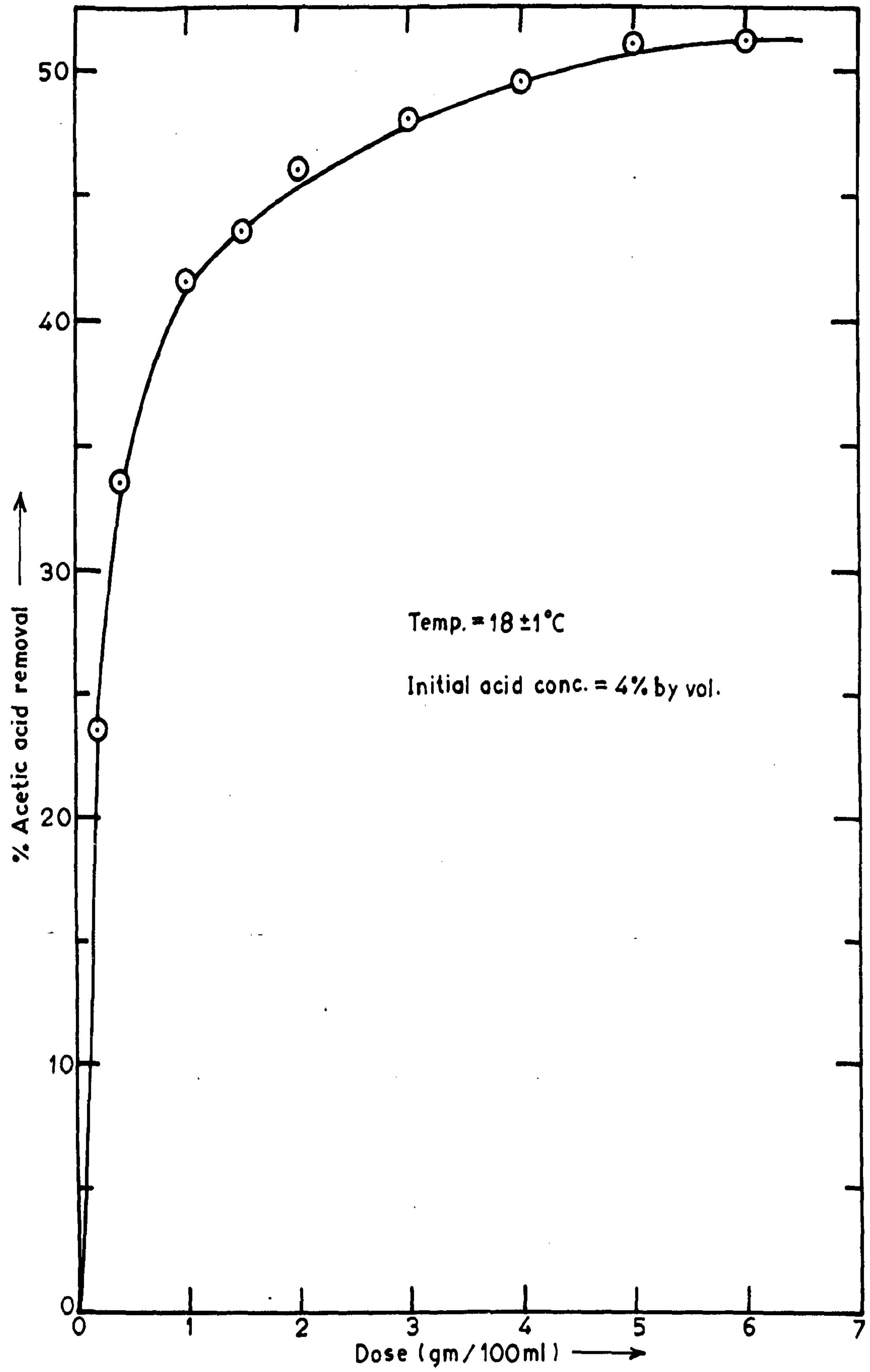


Fig.4.8. Effect of adsorbent dose (activated bagasse carbon).

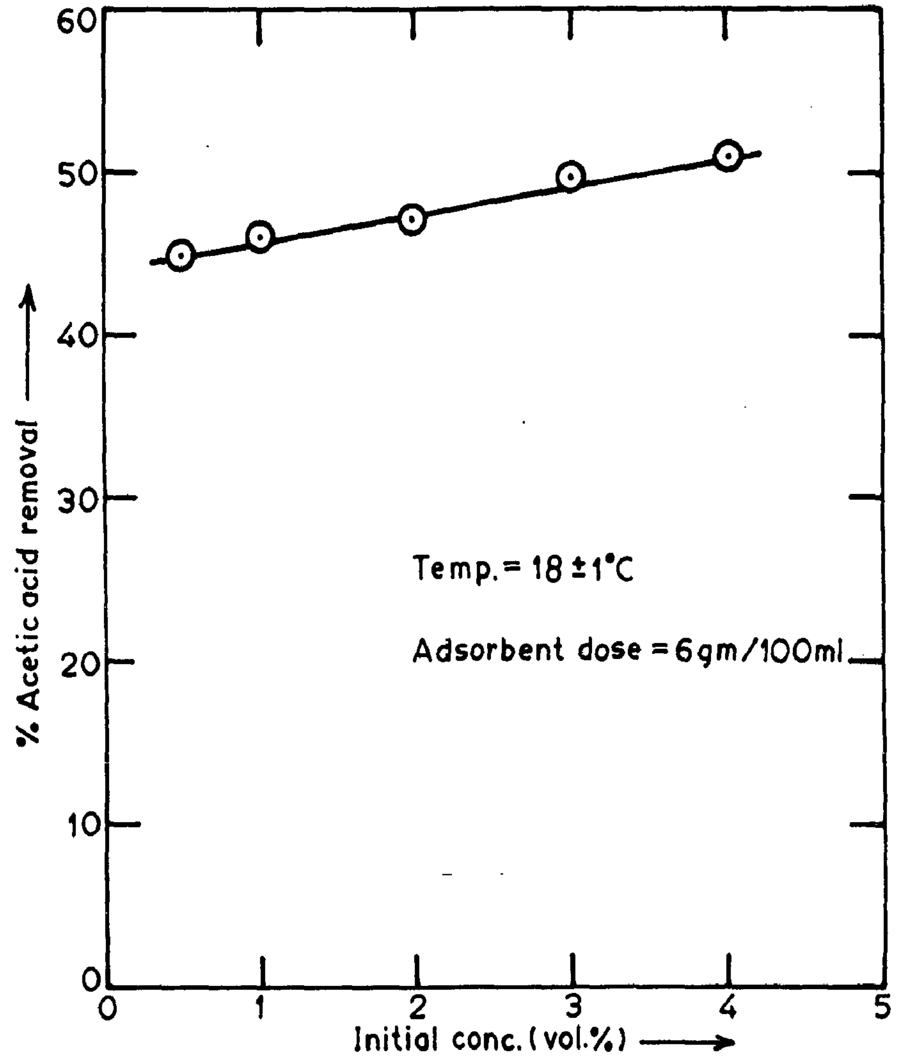


Fig.4.9 . Effect of initial acid conc. (activated bagasse carbon).

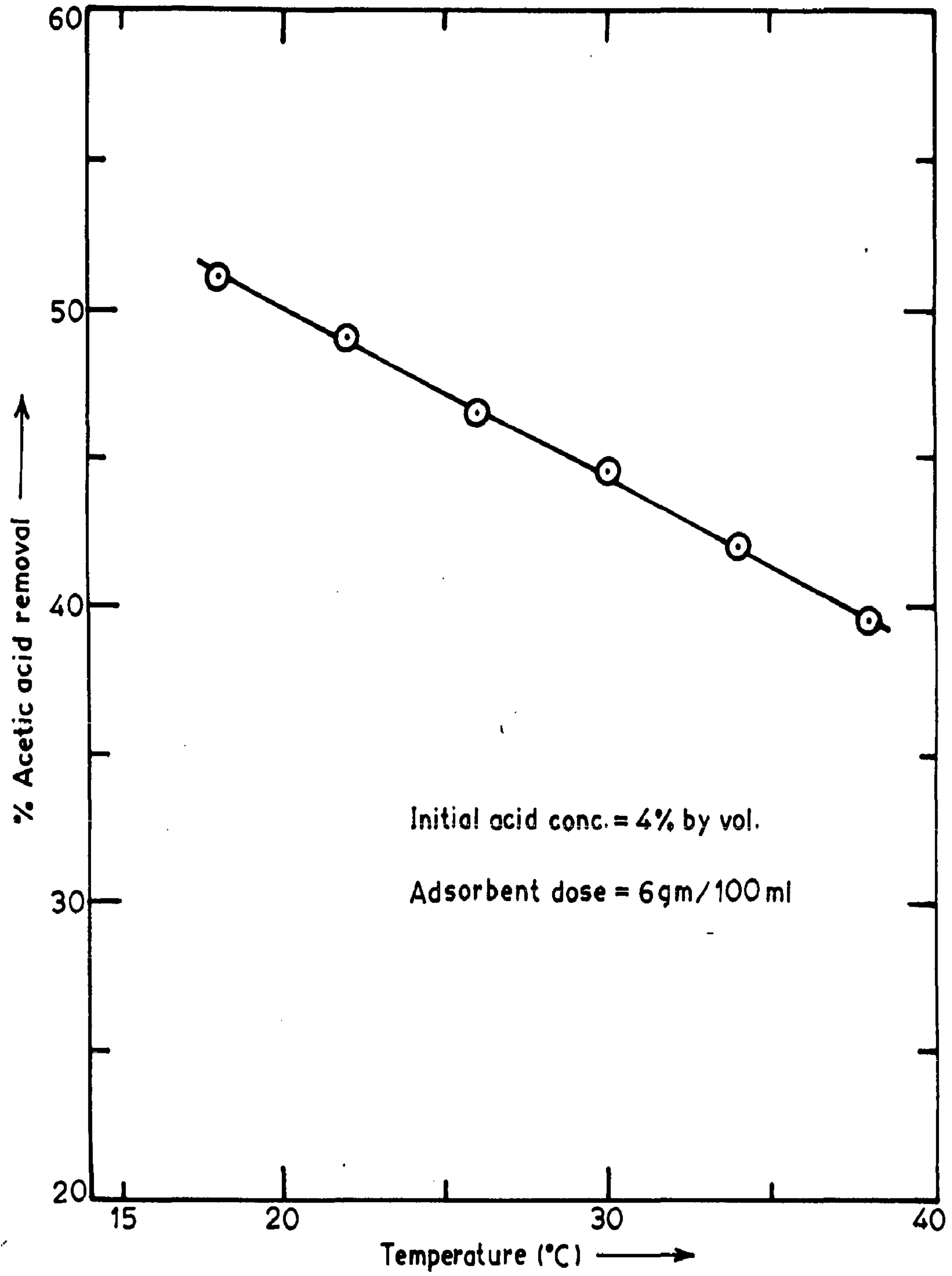


Fig.4.10. Effect of temperature (activated bagasse carbon).

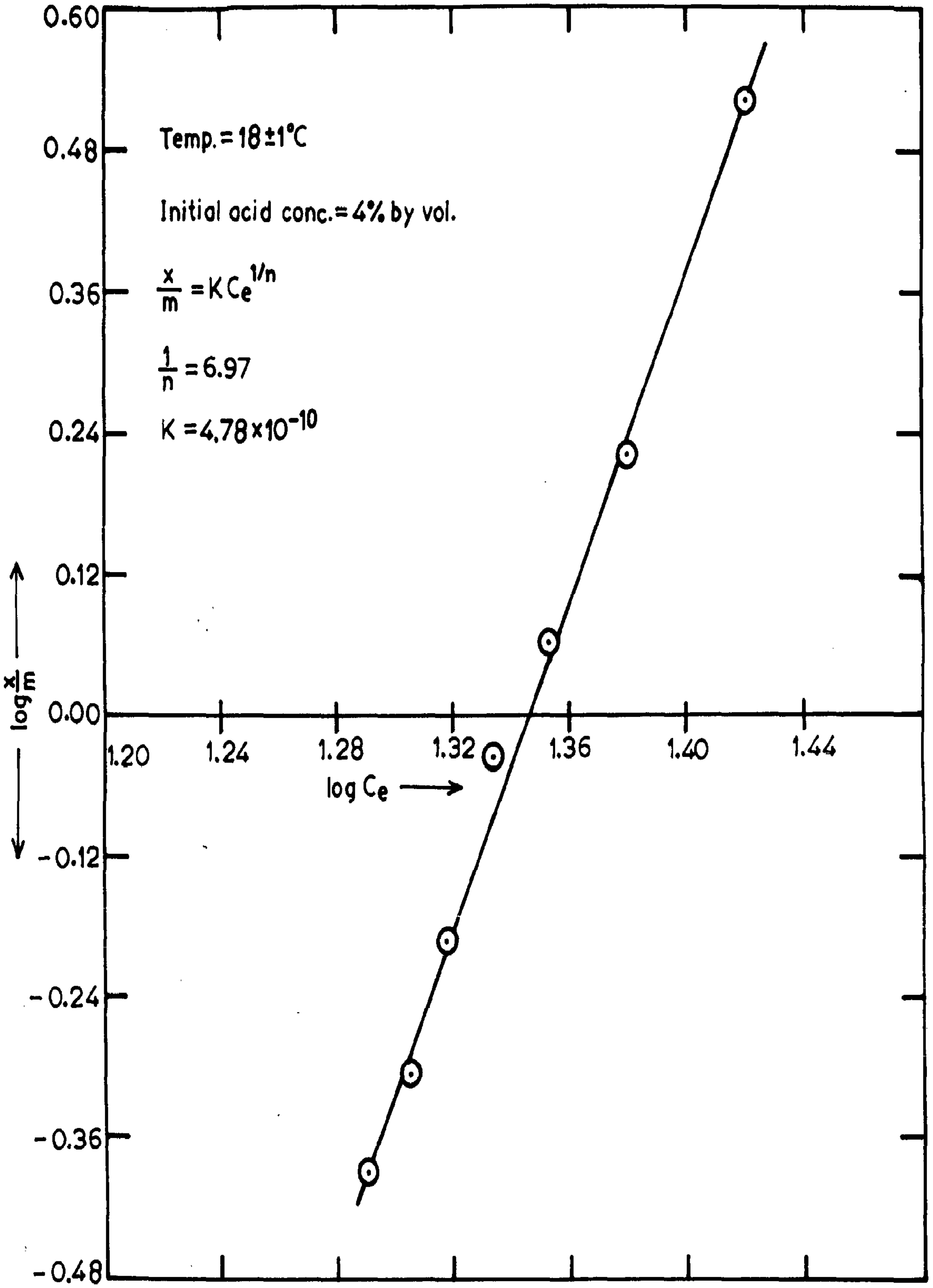


Fig.4.11. Freundlich isotherm (activated bagasse carbon).

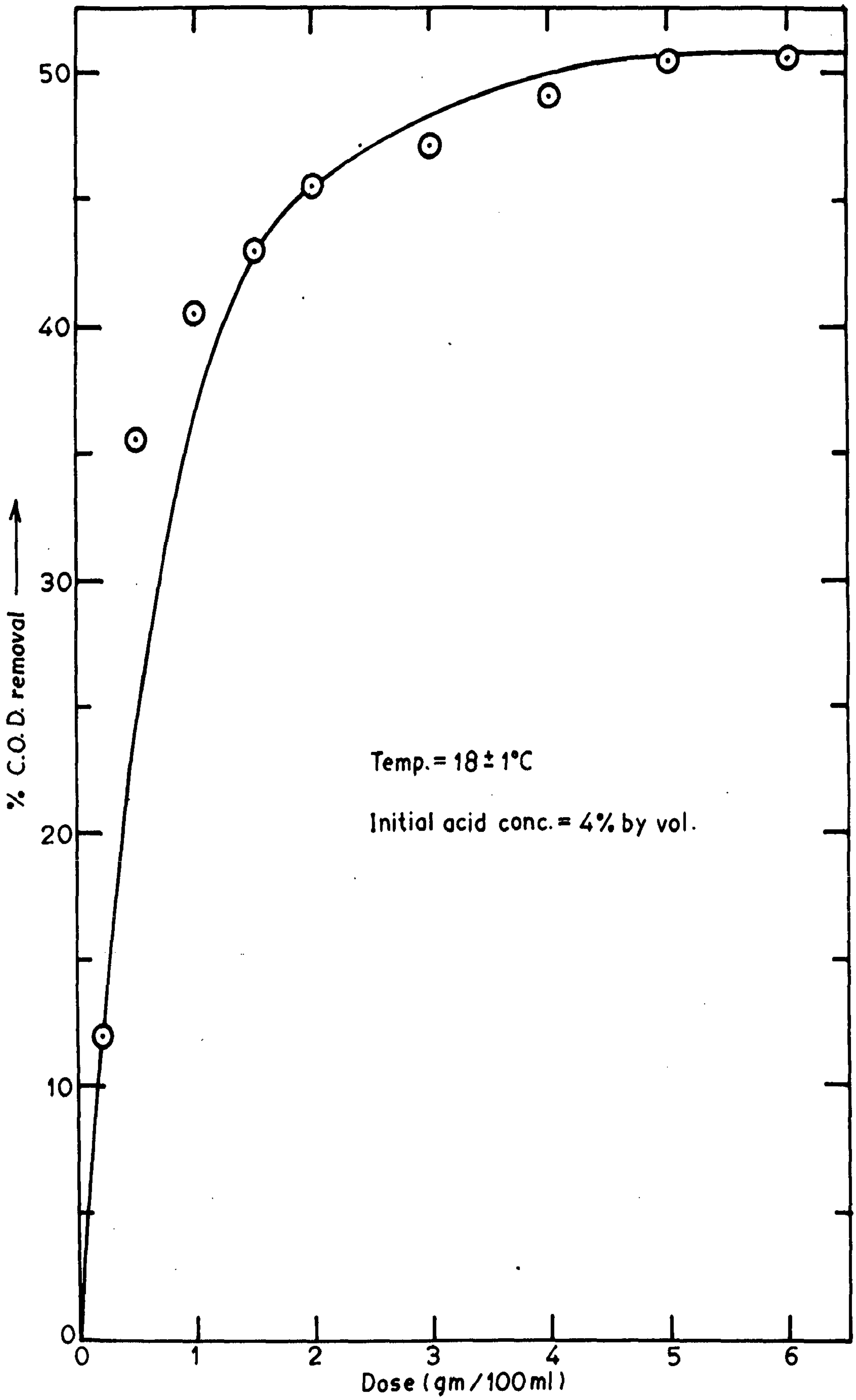


Fig.4.12. Effect of dose on % removal of C.O.D. (activated bagasse carbon).

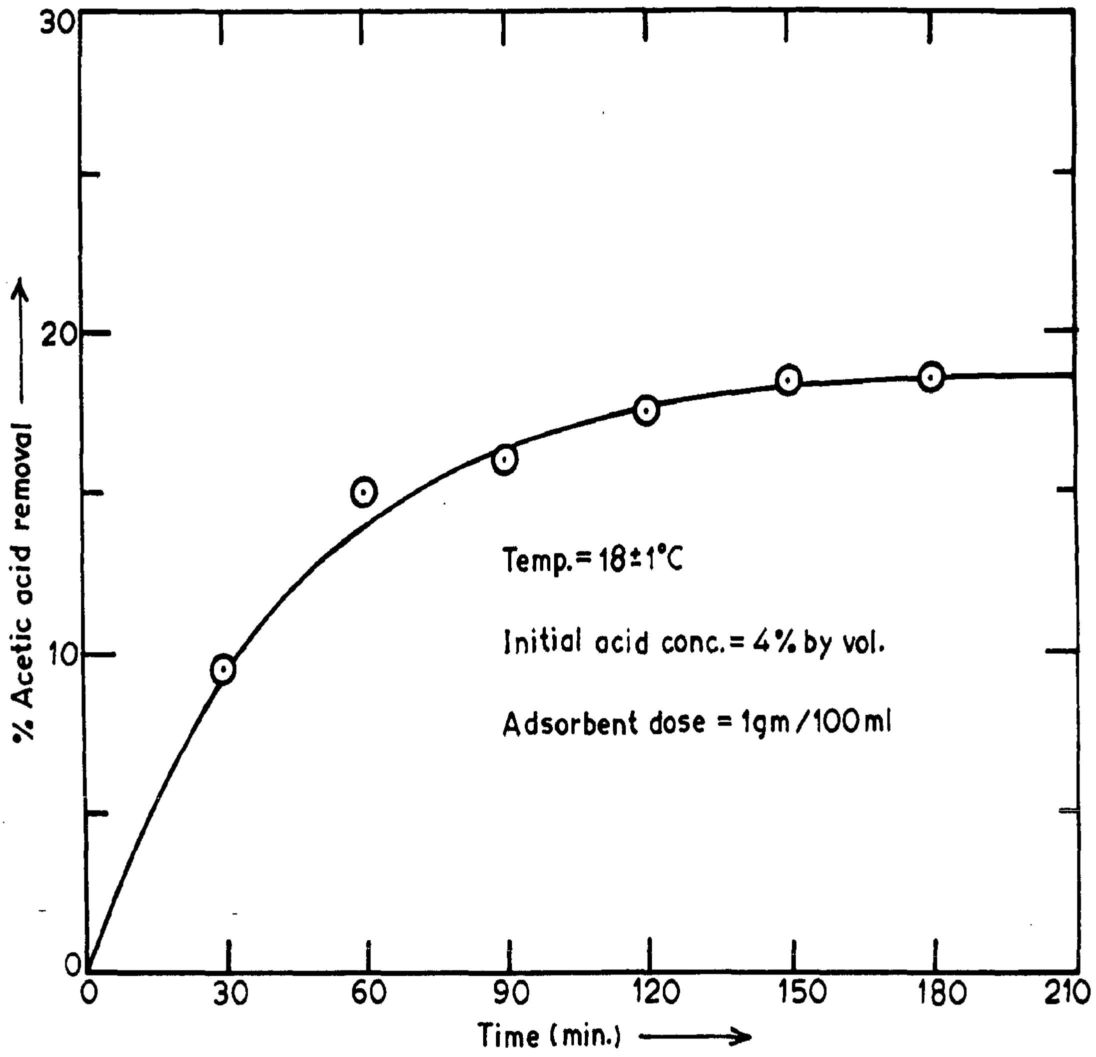


Fig.4.13. Equilibration time curve for activated saw dust.

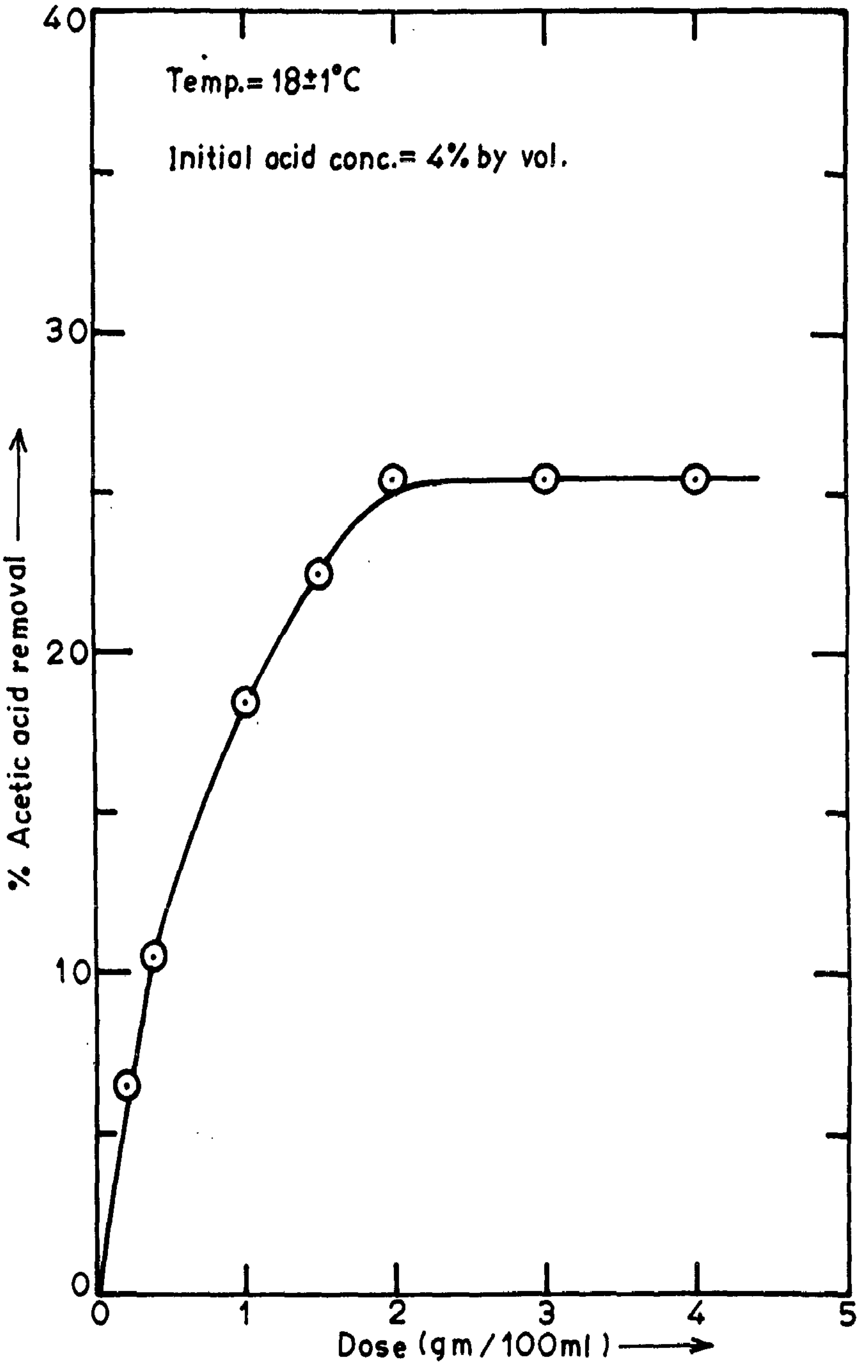


Fig.4.14. Effect of adsorbent dose (activated saw dust).

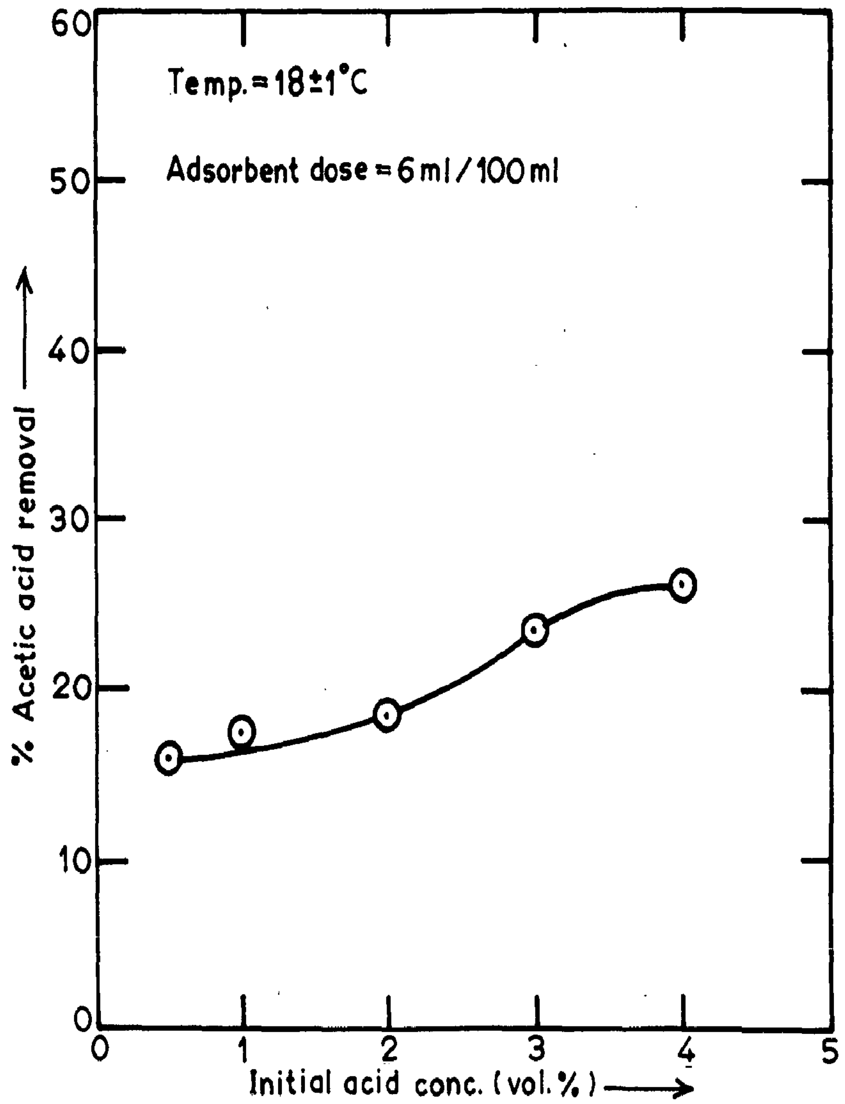


Fig. 4.15. Effect of initial acid conc. (activated saw dust).

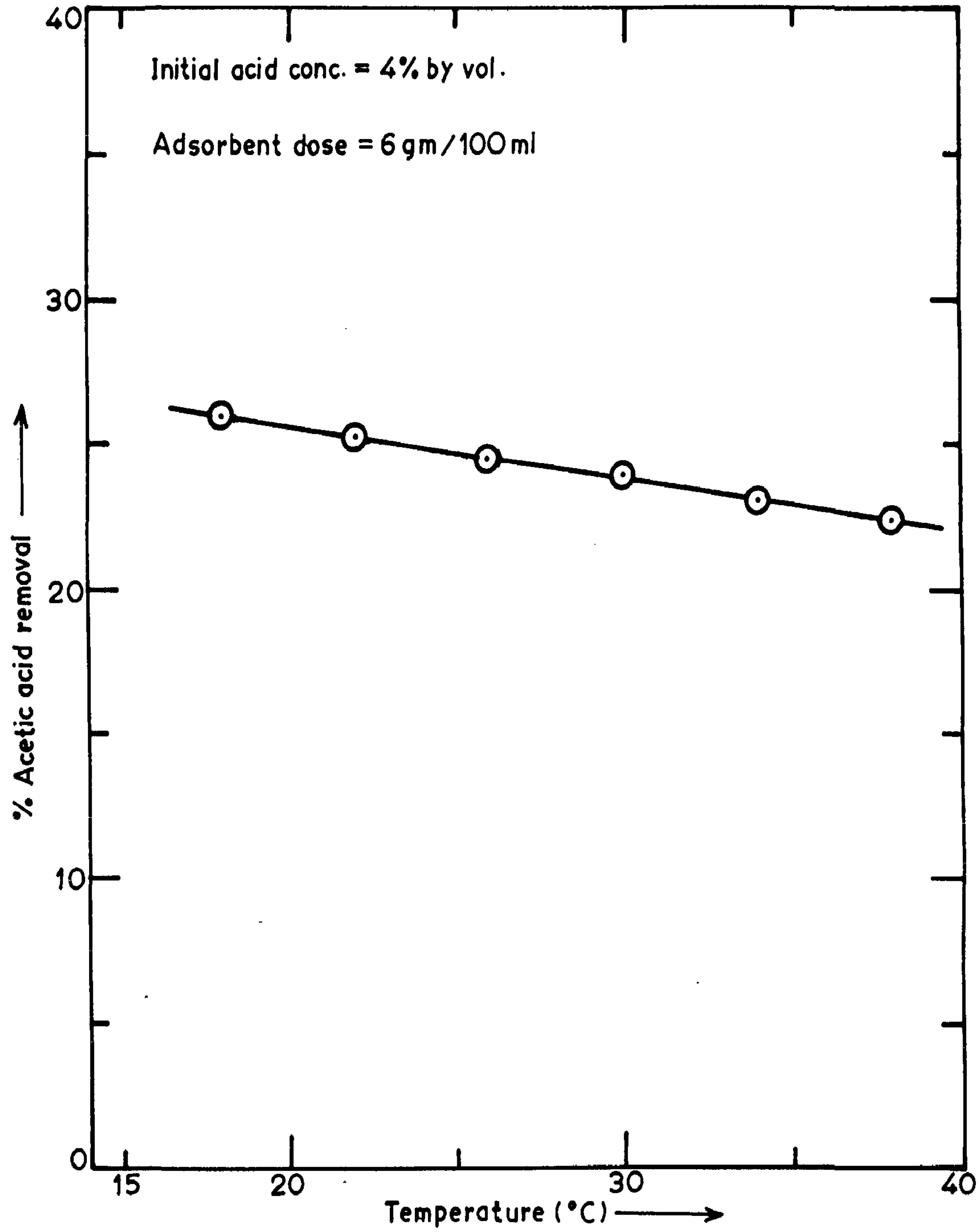


Fig.4.16. Effect of temperature (activated saw dust).

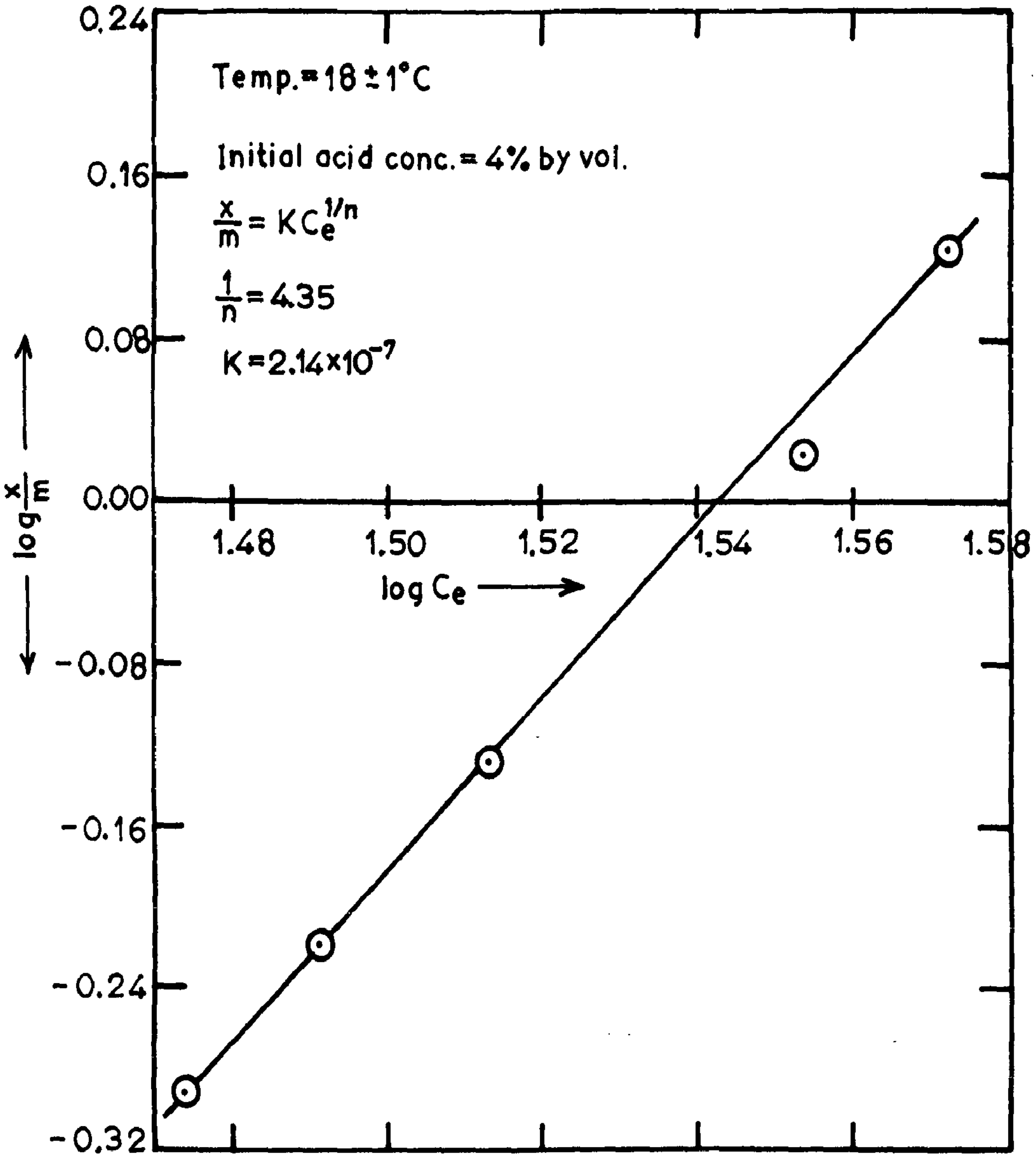


Fig.4.17 . Freundlich isotherm (activated saw dust).

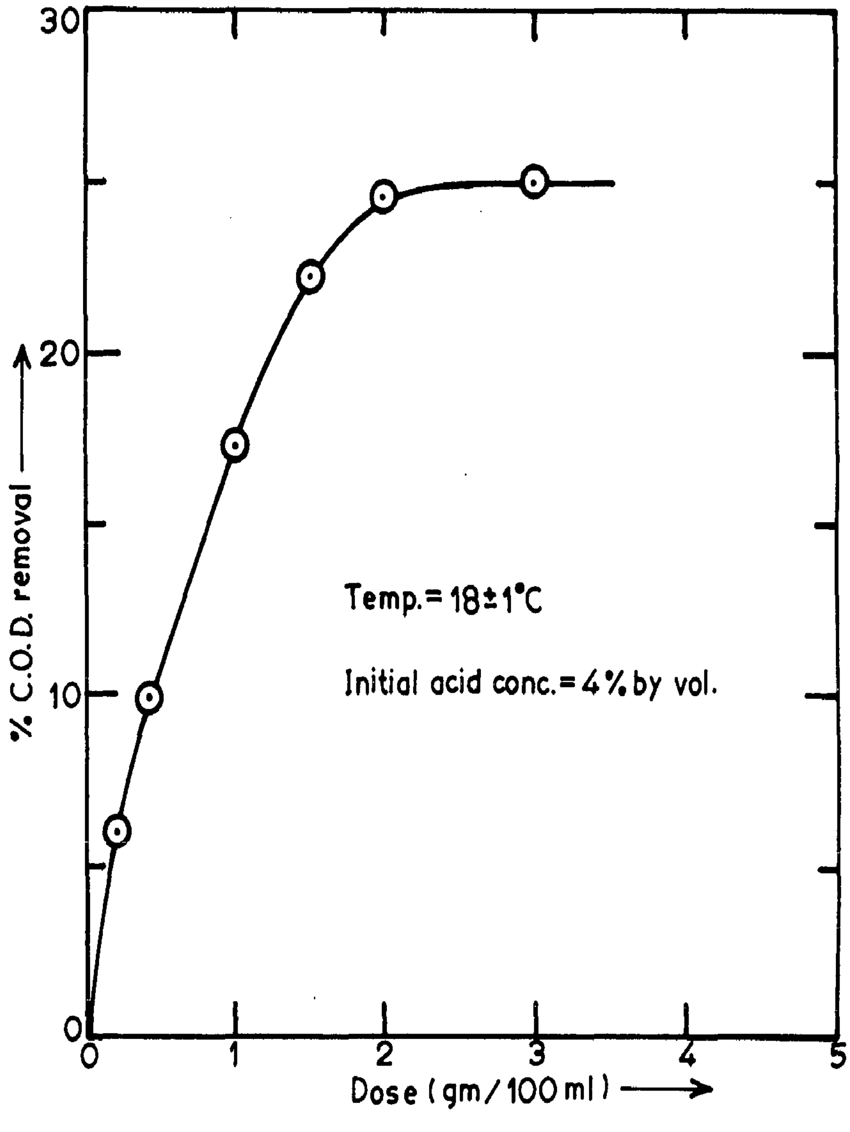


Fig. 4.18. Effect of dose on % removal of C.O.D. (activated saw dust).

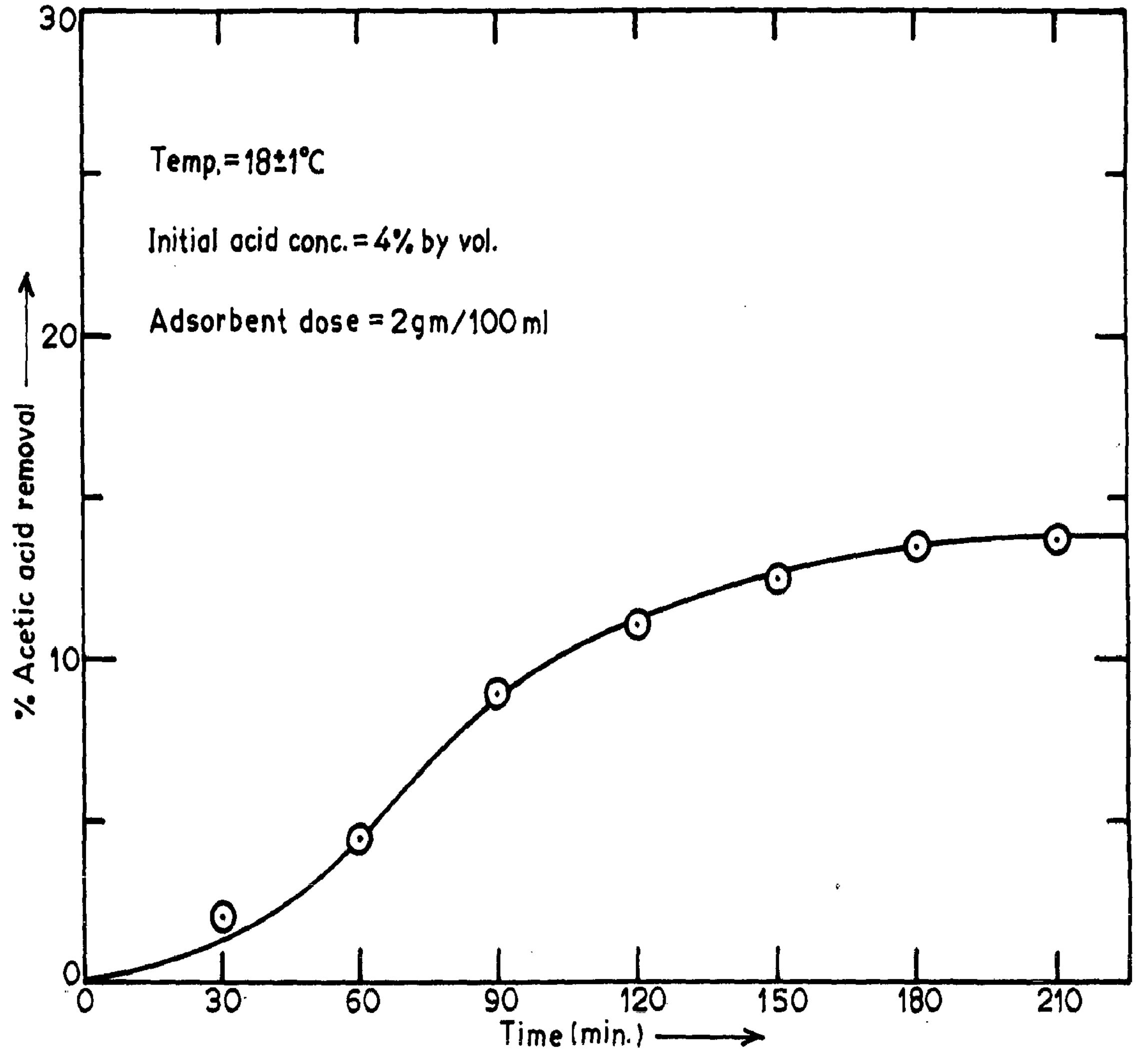


Fig. 4.19. Equilibration time curve for activated rice husk.

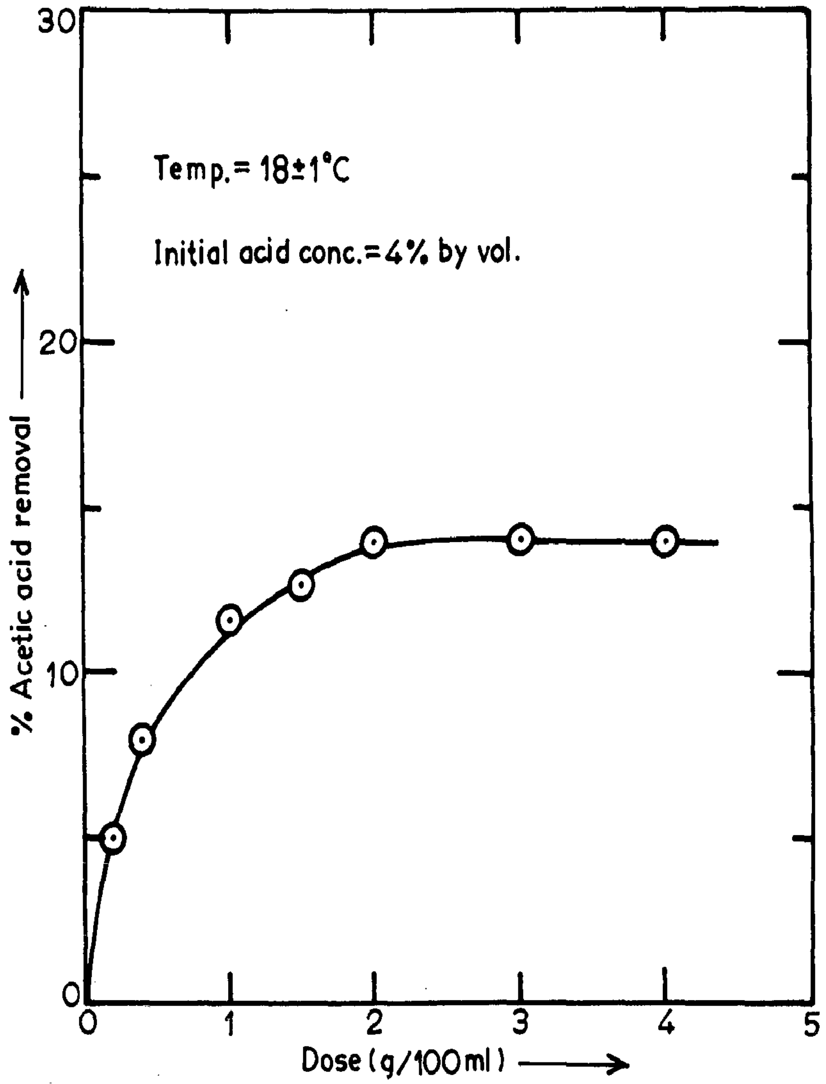


Fig.4.20. Effect of adsorbent dose (activated rice husk).

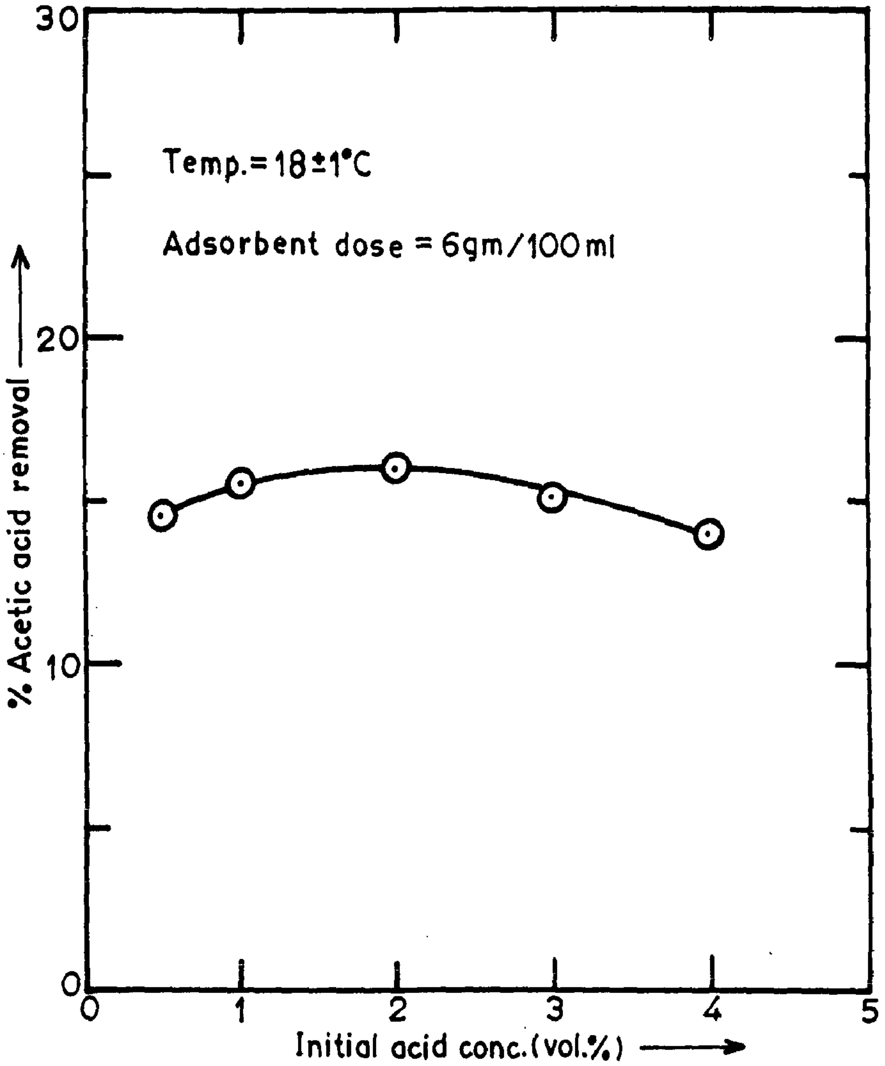


Fig. 4.21. Effect of initial acid conc. (activated rice husk).

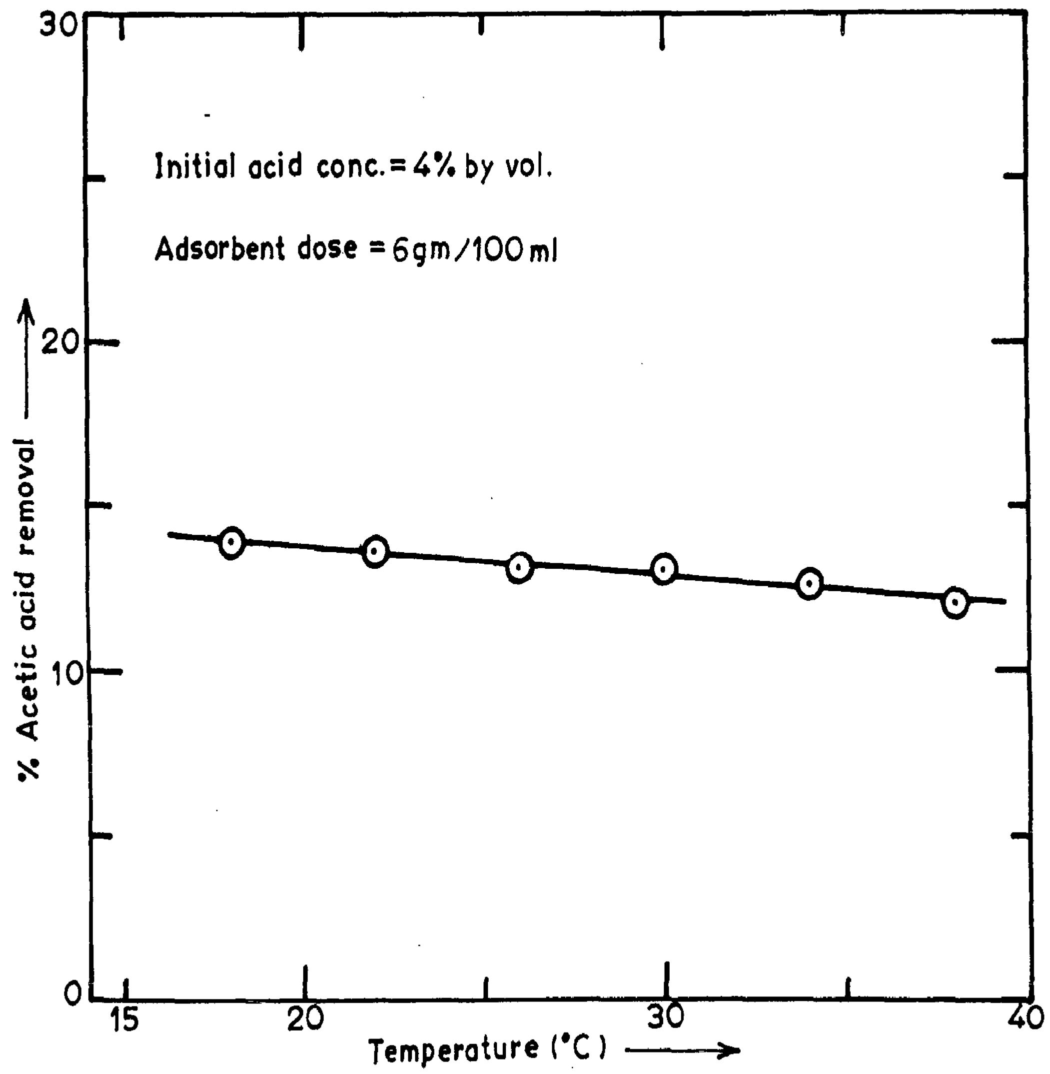


Fig.4.22. Effect of temperature (activated rice husk).

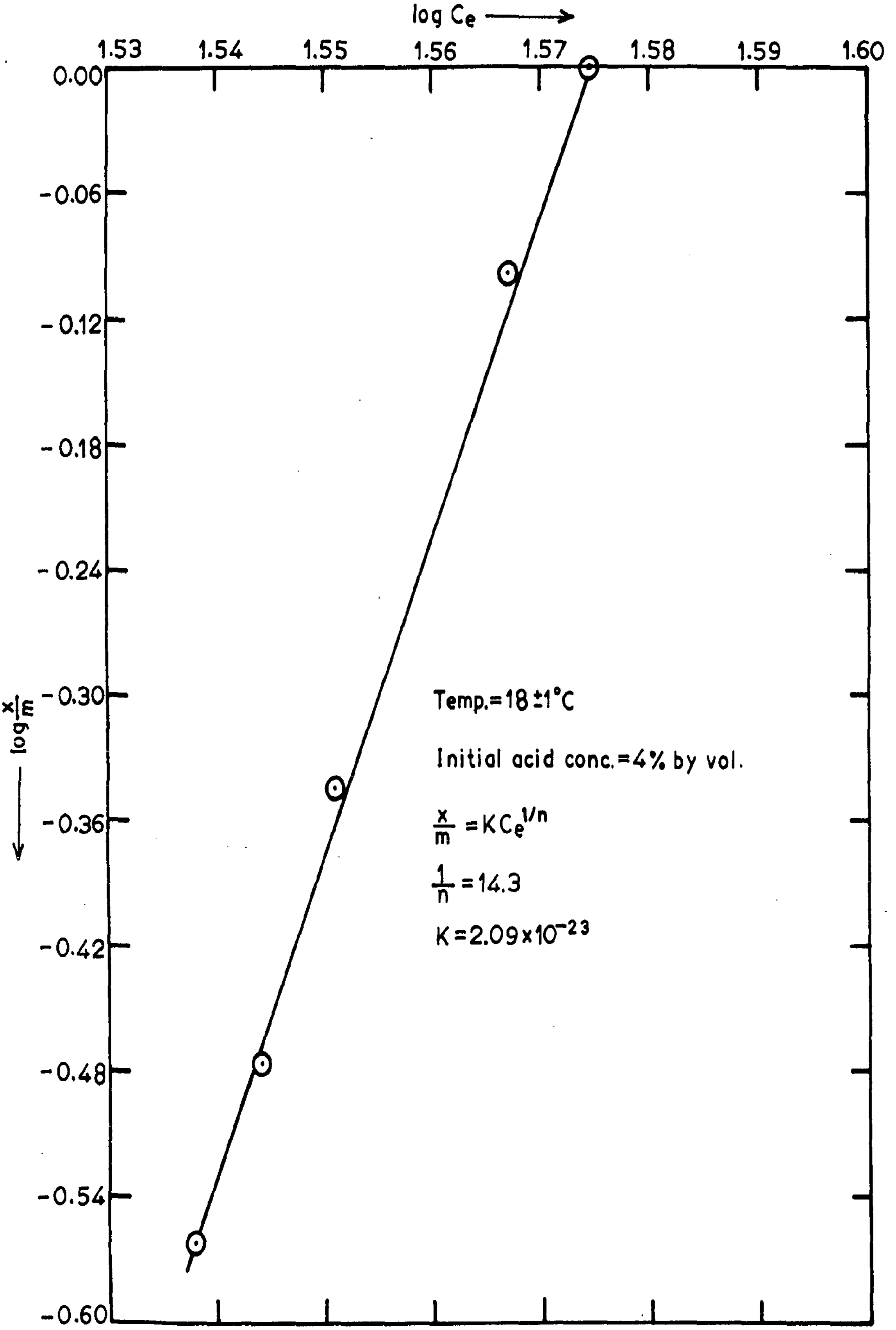


Fig.4.23.Freundlich isotherm (activated rice husk).

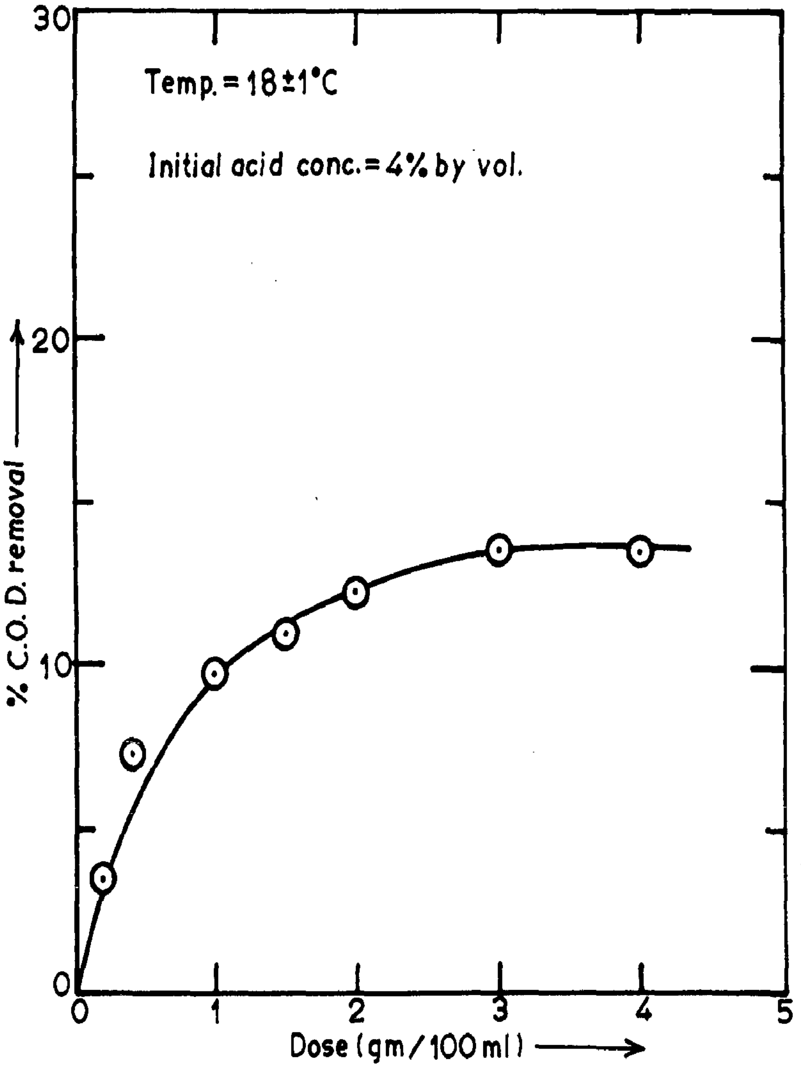


Fig.4.24. Effect of dose on % removal of C.O.D. (activated rice husk).

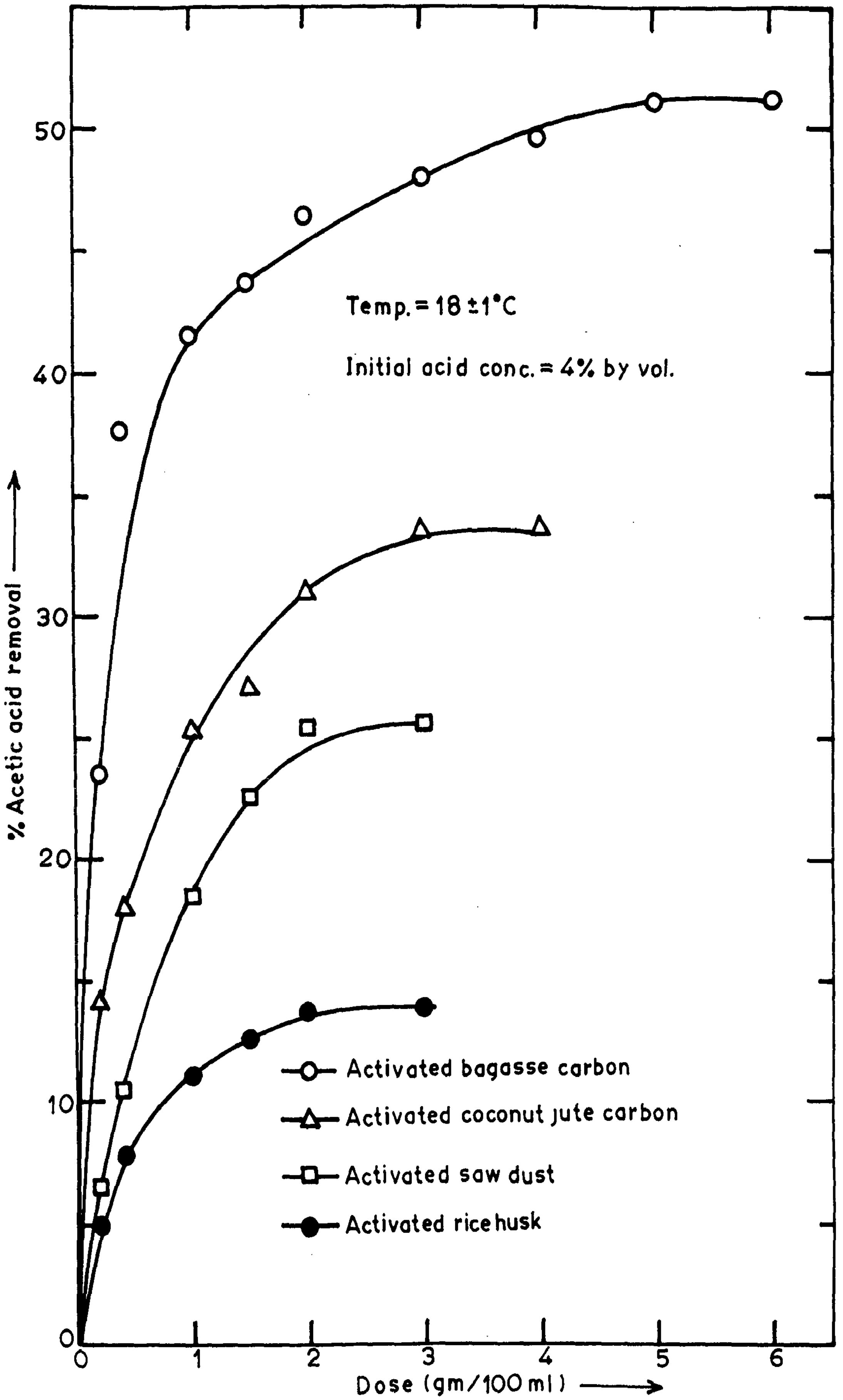


Fig.4.25. Effect of adsorbent dose (a comparative study).

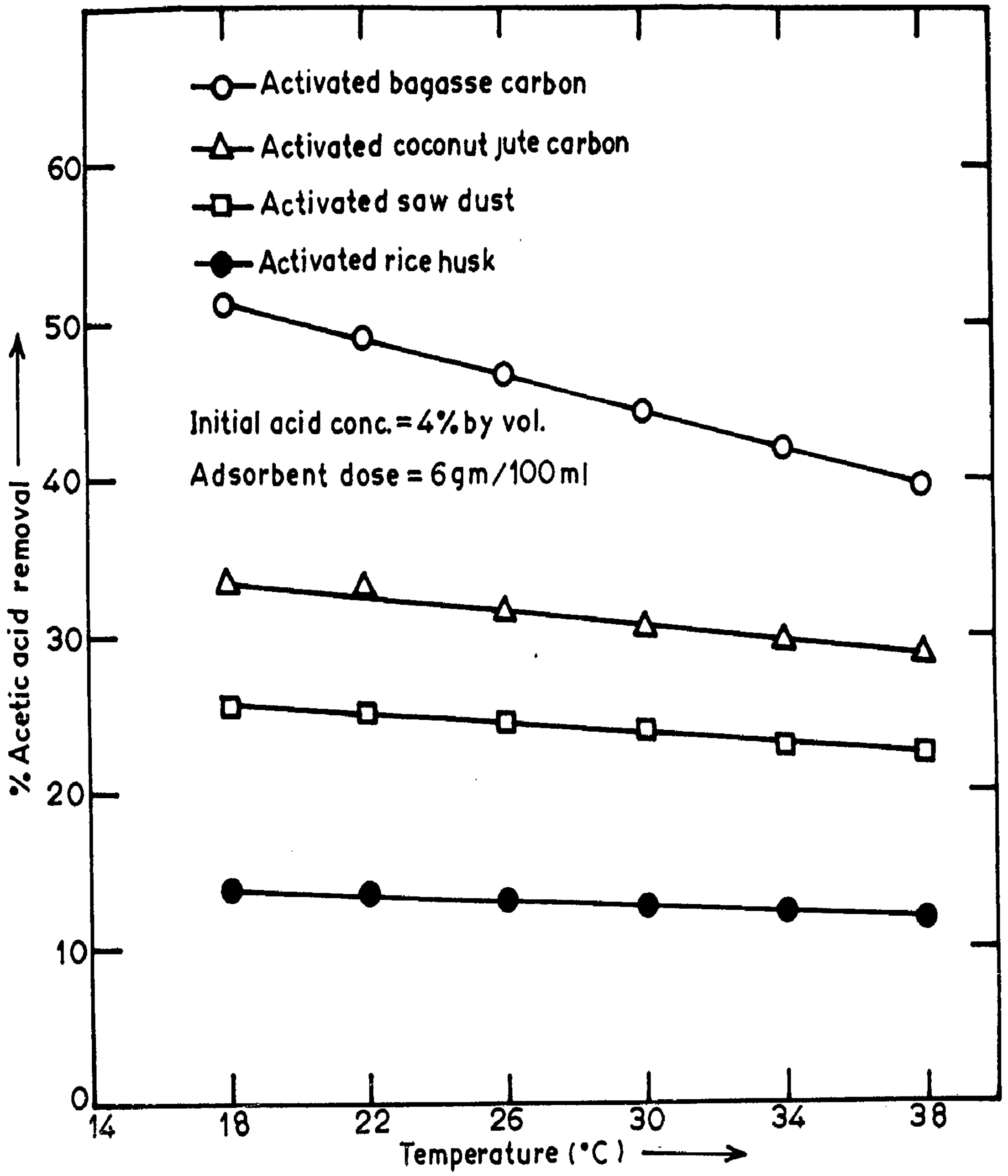


Fig.4.26. Effect of temperature (a comparative study).

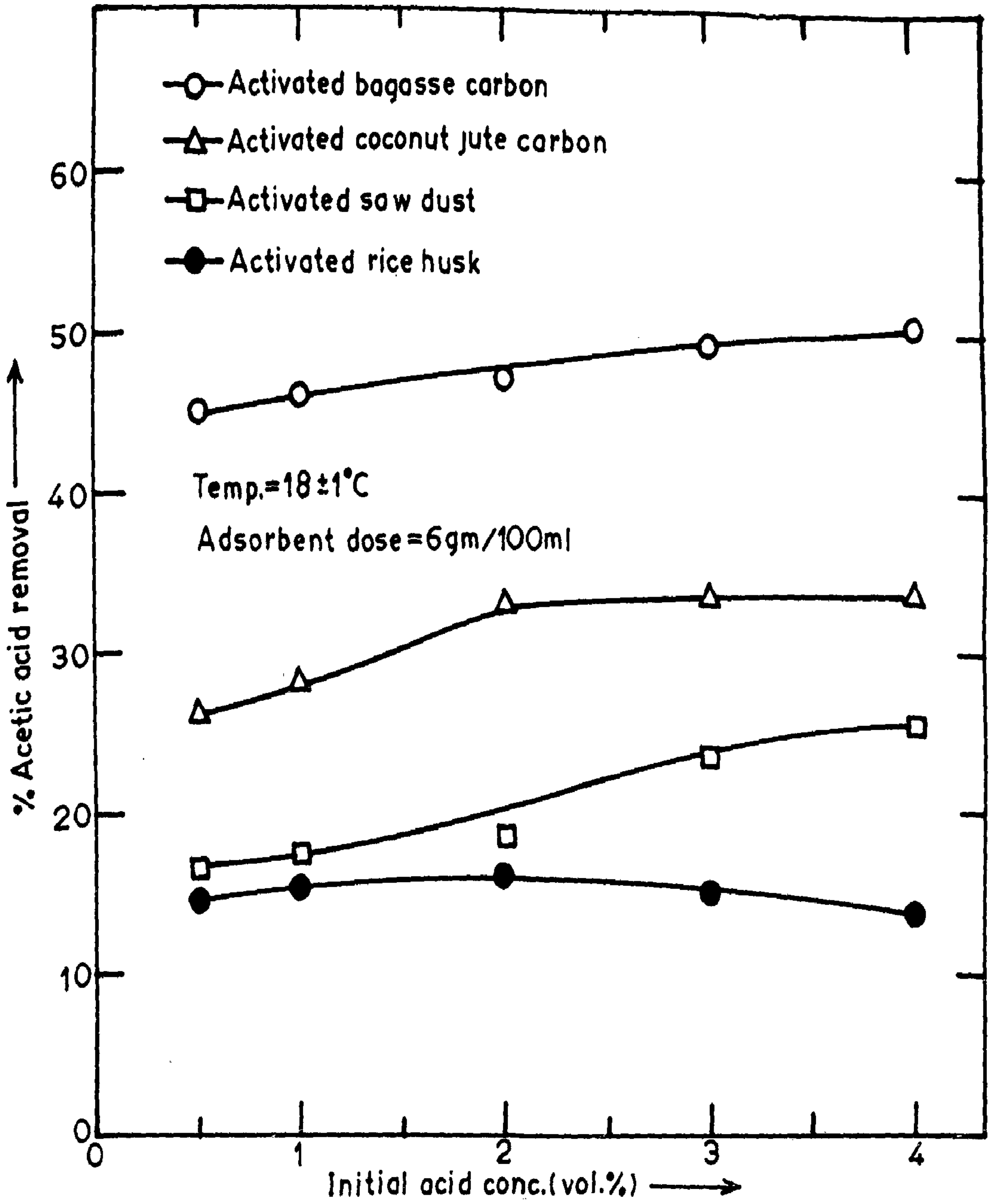


Fig.4.27. Effect of initial acid concentration (a comparative study).

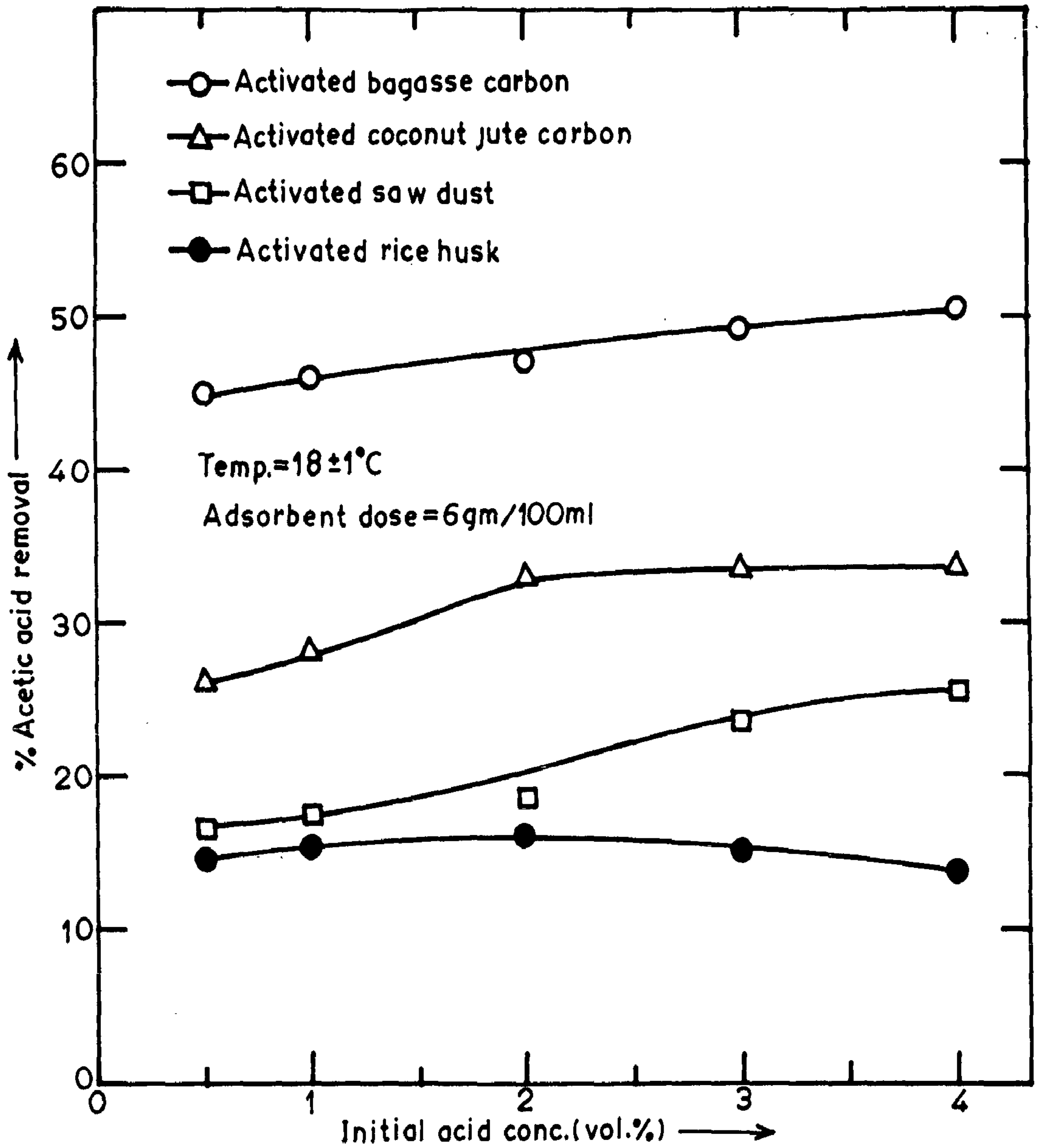


Fig.4.27. Effect of initial acid concentration (a comparative study).

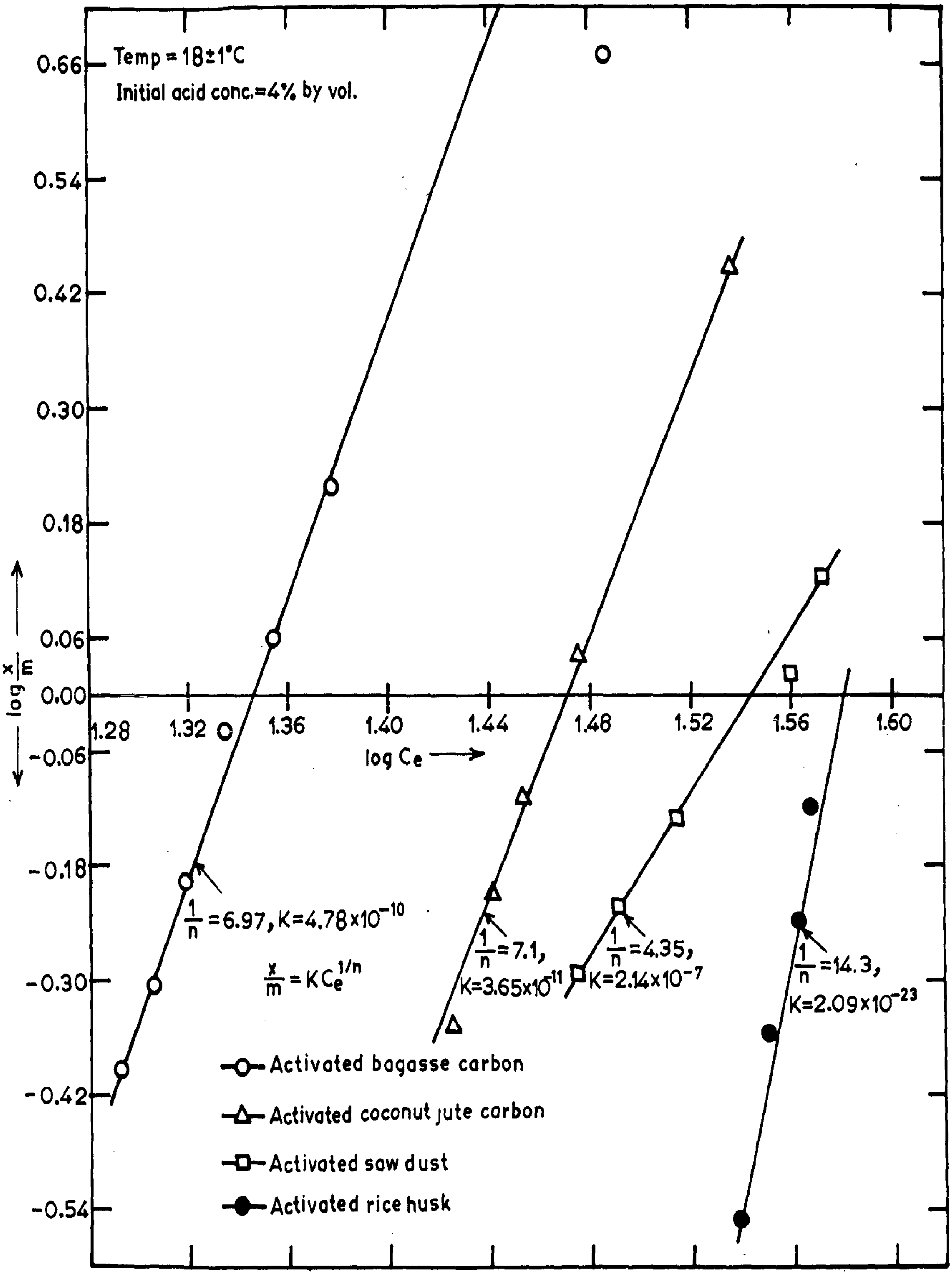


Fig. 4.28. Freundlich plot for comparative study.

CHAPTER V

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSION

(1) The results of the present study indicates that activated bagasse carbon is the best among the other adsorbents studied for the removal of acetic acid from the effluent of industrial waste. A maximum of 51.1% acetic acid can be removed from the effluent, containing 4% acetic acid at the room temperature ($18 \pm 1^{\circ}C$) using single batch reactor. However effluent containing acetic acid, can be treated successfully and the concentration of acetic acid can be brought down below the pollution control board limit by using no. of CSTR in series according to the need.

(2) The activity of activated bagasse carbon was also found to be comparably good for all the levels of temperature. A decline of around 18 - 23% in the activity level of all the four adsorbents has been observed when the temperature varied from 18° to $38^{\circ}C$.

(3) The adsorption pattern of all the adsorbents studied follow freundlich isotherm. Since the values of $\frac{1}{n}$(index of intensity) is in general greater than 1, it shows that the adsorbents (which are based on cheap agricultural materials) are not very good for the adsorption of acetic acid. However, it can be successful, economic removal process of acetic acid from

liquid effluent if We use these cheap agricultural materials as adsorbents in series.

RECOMMENDATIONS

(1) Based on present studies and having considered its economic aspects, it is recommended that the activated bagasse carbon may be used commercially, if used in multiple contact, since the activity of activated bagasse carbon is comparably high for a wide range of initial acetic acid concentration and temperature for the removal and recovery of acetic acid from the industrial effluent.

(2) One can reduce the C.O.D. level of Industrial waste containing carboxylic acid by using activated bagasse carbon as adsorbent successfully.

(3) Since in the present studies, synthetic waste water was used in order to avoid interference by the other metal, ingredients present in the actual waste water, it is recommended that further studies should be under taken to explore the possible effects of these materials on the adsorption process.

REFERENCES

1. Morrison R.T. & Boyd R.N., Organic Chemistry (1969) Prentice-Hall of India Private Limited, PP.578-582.

2. Standard Methods for the Examination of Water & Waste Water (1976) by American Public Health Association, American Water Works Association & Water Pollution Control Federation.

3. Minear. R.A. & Keith, L.H., Water Analysis. Organic Species Vol.III (1984), Academic Press. New York.

4. A Project Report on Manufacturing of Actefic Acid by Gas Authority of India Limited (1990).

5. Prespective Plan for Chemical Industry (Upto Yr 2000 A.D.) Report on the Organic Chemical Vol.3 by Department of Chemical & Petrochemical. Gov. of India.

6. S.R. Sharma, Rathore, Ali & Ahmed (1985) Adsorption of Carboxylic Agrochemicals from Saline Water, Indian J. Environ. Health. Vol.27, No.2, PP 130-139.

7. Antonio A. Gracia King (1989). The Use of Basic Polymer Sorbent for the Recovery of Acetic Acid from Dilute Aqueous Solution, Ind. Eng. Chem. Res., 28, PP. 204-212.

8. K.J. Himmelstein (1974), Removal of Acetic Acid from Waste Waters, Engineering Bulletein of Purdue University, PP. 677-689.

9. IS:3025-1964, Indian Standard Methods of Sampling and Test (Physical and Chemical) for Water Used in Industry ,Indian Standard Institution.

10. Mcketta, J.J., Encylopedia of Chemical Processing and Design (1976), Vol.2, March Dekker Inc., New York.

11. Kirk-Othmer Encylopedia of Chemical Technology, Edited by Mark, Mcketta & Othmer, Interscience Publishers, New York, Vol.1, PP.422-463.

12. Linsen, B.G., Physical and Chemical Aspects of Adsorbents and Catalysis. Academic Press London and New York.

13. Clark Alfred, The Theory of Adsorption and Catalysis 1970, Academic Press, London and New York.

14. M.E. Thesis, "Removal of Dye from the Waste Water", by H.R. Ghatak, University of Roorkee (1991).

15. Bisarya S.C. & Patil D.M. (1993) Determination of Salicylic Acid and Phenol (PPM level) in Effluent from Asprin Plant, Research & Industry 38, PP.170-172.

16. George F. Rohrich, Environmental Management (1994), Balinger Publishing Company, Cambridge, Masshusetts.

17. Krishna Kewal, "Environmental Pollution and Public Health-Legal and Administrative Aspects",(Memographed).

18. Manual on Waste Water Analysis NEERI.

19. Bhattacharya, A K. and Venkobachas, C. (1984), Removal of Cadmium by Low Cost Adsorbants. Journal of Env. Engg. 110(1), 110-122.

20. Webber W.J. Jr. (1972), Physico Chemical Process for Water Quality Control, Wiley Interscience, New York.

21. M.E. Thesis "Removal of Chromium from Waste Water", by Pavan Kumar, University of Roorkee, (1993).