Adsorption of Chromium (VI) From Tannery Effluents - Comparison of Adsorbents

By

V. Sharulatha

A DISSERTATION SUBMITTED TO THE AVINASHILINGAM INSTITUTE FOR HOME SCIENCE AND HIGHER EDUCATION FOR WOMEN - DEEMED UNIVERSITY, COIMBATORE - 641 043
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Certified As Bonafide Research Work

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Introduction

1.INTRODUCTION

AIR IS THE VITAL FORCE
WATER THE PROGENITOR
THE REST EARTH IS THE MOTHER OF ALL

Man in his quest for comfort, weather and power has been ignoring nature's law and broken out the circle .In the process of achieving these, man has been constantly changing the basic characteristics of his environment by (i) removing some of its essential components (ii)adding on some undesirable components (Jain &Jain (1984))

The term environmental pollution refers to a situation in which the outdoor ambient atmosphere contains species capable of causing harmful effects to man and his environment (Renu Kumar 1989) The term pollutant means any chemical, agrochemical substance or biological product capable of polluting the natural environment of man and other living organism. At present, water pollution needs immediate attention due to rising population, rapid urbanization and growing industrialization. Human and animal waste lead to water pollution in the economically poor countries but in the rich nation it is found to be due to extravagant life style and multivaries establishments of widespread industries owing to the discharge of industrial effluents into natural bodies of water with out any prior treatment, many of the major Indian rivers are found to be highly polluted .As a result of water pollution, the stream fails to exercise the self purification process due to depletion of oxygen.

Owing to its huge animal population India stands first in the world in producing `hides and skins. There are about 2000 tanneries in India mostly spread over Tamilnadu, West Bengal, Uttar pradesh and Andhra pradesh (Agarwal 1996)

Recently the tanning industries have switched over to 'chrome tanning ' from vegetable tanning. Large amounts of chromium sulphate are used in this process resulting in the heavy metal concentration in effluents leading to chromium pollution (Sastry 1990). Though highly essential in microquantities for biological activities, chromium is hazardous at higher concentration.

The removal of chromium from these effluents have been reported through several methods such as (i)reduction (ii) precipitation (iii) ion exchange (iv)reaction with silica (v) electrochemical reduction (vi)evaporation and (vii) reverse osmosis.

But most of these methods need high capital cost and recurring expense such as chemicals, which are not suitable for small-scale industries. Recently studies in the treatment of tannery effluent by adsorption on activated carbon have revealed it as a highly effective, cheap and an easy method among the physico chemical treatment processes. Although adsorption on activated carbon is effective, owing to the highest cost and difficulty in procurement of activated carbon efforts are being directed towards finding out efficient and low cost adsorbent like fly ash, wood charcoal,bituminous coal,lignite coal, rice husk carbon etc.

1.1.Objectives

In the present work, three adsorbents namely raw saw dust (a waste material in timber works), carbonised saw dust and carbonised bagasse (a waste material in sugar cane industries and sugar cane juice shops) were used as the adsorbents in the removal of Cr. (VI) from tannery effluent. The objective of this work are

(i) To gain insight into the conditions for the adsorption of Chromium (VI) on the 3 adsorbents - adsorbent dosage and effect of pH.

(ii) To compare their performances in the adsorption of Chromium (VI).

Review of Literature

2.REVIEW OF LITERATURE

2.1.a **Tanning** is the process of conversion of animal skins and hides to non-putrescible and tough material known as leather .The tanning processes are broadly classified as

a) Beam house processing and

b) Tanyard processing

a) BEAM HOUSE PROCESSING

The dry matter of the skin is almost protein reported to be about 85% collagen. The skin also contains lipids, albumin,carbohydrates and globulin in minor amounts. In beam house processing all the impurities are removed and collagen of the skin is made ready to absorb the tannin or chromium.

b) TANYARD PROCESSING

There are two types of tanning

I)Vegetable tanning II) Chrome tanning

I) VEGETABLE TANNING

This type of tanning produces heavy leather and they are less affected by changes in humidity and body perspiration.

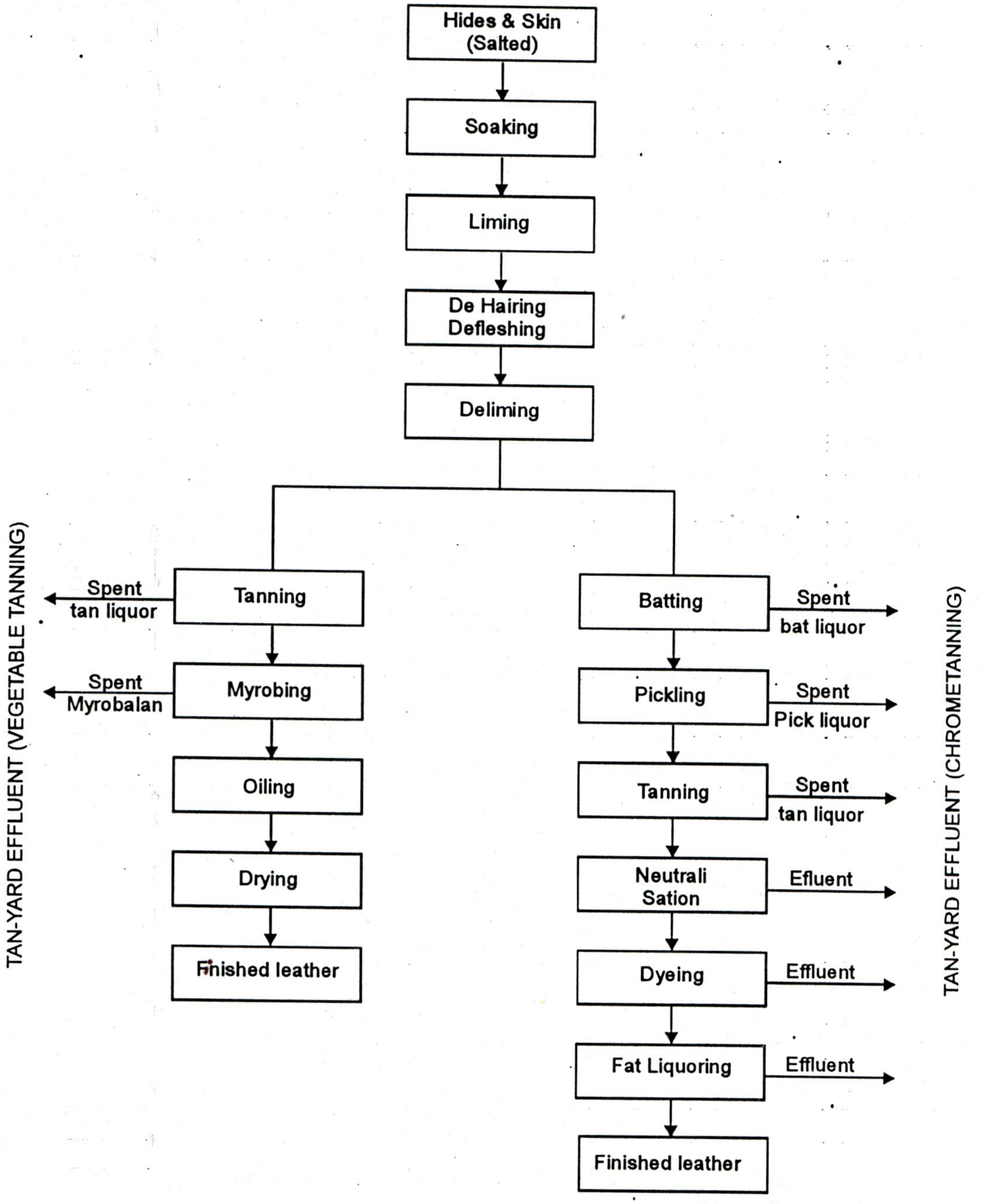
The delimed skins and hides are soaked for 10-15 days in pits containing vegetable tan liquor which comprises vegetable substances (extracts of bark, wood, nut etc., containing natural tannin) and also pyrogallol or catechol bases. The tanned material is then subjected to myrobing oiling and then dried and dyed (Manivasakam 1984) flow chart for process of tanning has been listed in figure-1

II) CHROME TANNING

The pickled skins and hides are subjected to chrome tanning, employing solutions of basic chromium sulphate or chloride (10 % of the total weight of raw hide).Chrome tan mixture is prepared from mixtures of dichromate and sulphuric acid reduced with glucose or molasses or similar organic materials.The process takes about 6 hours .At the end of the process $Na_2 Co_3$ (8 % by weight of raw hide) is added to facilitate proper reaction of the chromium with the proteins of the hides .The tanned hides and skins are then taken out and piled and allowed to remain for 24 hours for complete adsorption and fixation of chromium (Dr.Agarwal 1996)

FIG. 1

FLOW CHART OF TANNING (VEGETABLE & CHROME)



2.1 b. CHARACTERISTICS OF CHROME TANNING EFFLUENT

This is the toxic fraction of tannery effluent and contains excess chromium (in trivalent state) ranging from 100 –200 mg/l .It has a characteristic chrome green colour, acidic in nature with B·O·D of about 1000mg/l (Manivasagam -1984)

Average composition of spent chrome tan liqueur are listed in table –1(Narayana Rao-1987)

The characteristic of tannery effluent as studied in 1975 is given in table –2(Varshney-1983)

Roughly estimated the worldwide consumption of chromium by leather industries is about 15000 tonnes/year which is about 2.5 % of the total consumption. Approximately 32,000 tonnes of basic chromium sulphate salts are consumed annually by Indian tanneries in the process of tanning. Only 65-70 % of chromium is taken up by the hide /skin and the rest goes into the waste stream. The chrome laden waste produced from large and small scale tanning industries if treated in India will produce about

TABLE –1

Average composition of spent tan liquors [vegetable & Chromium] in a typical Indian Tannery [Chakravarty ETAL]

S.no	item	Spent vegetable tan liquor	Spent chrome tan liquor
1	pH	5.4	3.2
2	alkalinity as Caco 3 mg/l	----	-----
3	acidity as Caco3 mg/l	2560	5400
4	chloride as Cl mg/l	3000	7200
5	Total solids mg/l	34800	7480
6	suspended solids mg/l	2660	705
7	cod mg/l	30240	3584
8	bod	16000	-----
9	Cr. mg/l	-----	2800

TABLE –2

CHARACTERSTIC OF A TANNERY EFFLUENT IN INDIA

s.no	characterstic	Limit
1.	pH	9.5
2.	Suspended solids (ss) mg/l	3200
3.	BOD 20 C mg/l	7000
4.	COD mg/l	------
5.	Chromium mg/l	15.20

(Course manual on Industrial treatment NEERI 1975)

25,000 tonnes of chrome bearing solid sludge per annum (Prasad and Unninair 1994)

Traditionally people collected the solid wasteland sludge from tanneries (during vegetable tanning) for application in grape gardens and this practice is continued even now in acid laterific soils. However with the switch to chrome tanning solids sludge began accumulating in most of the tanneries, because the waste become unsuitable for land application partly because of the presence of chromium salt (the Hindu Feb-4 1998).

2.2 TOLERENCE LIMIT OF CHROMIUM

There are two predominant forms of chromium;cr^{3+} and $cr.^{6+}$ which are found in tannery effluent (Varshnery-1983).The maximum tolerence limit for total chromium for public water supply has been fixed as 0.05 mg/l as per Indian standards (Hardamsingh Azad 1974)

Specific tolerance for effluents of chrome tanning industry is given in table –3 (Manivasagam-1984).

Table-3

Specific Tolerence for Effluents of Chrome Tanning Industry

S.no	Characterstic	Tolerence limit
i)	Chlorides (as Cl) mg/l	1000
ii)	BOD (5 days at 20 C) mg/l	30
iii)	Hexavalent Chromium mg/l	0.1
iv)	pH	5.5 to 9.0

The above table is reproduced from "I S 2490 (part- III) 1974, Tolerence limits for Industrial effluents .discharged into Inland surface waters (part-I) Tanning Industry (First revision)"

2.3 TOXIC EFFECTS OF CHROMIUM

2.3. a) EFFECT ON AQUATIC SYSTEM

When the chromium containing effluent enters the rivers, the trivalent chromium present in the effluent has taken the oxygen in the medium. This leads to the inversion of trivalent chromium to hexavalent chromium. The hexavalent compounds however are strong oxidising agents and they are much toxic due to their irritant and corrosive properties and their higher rate of absorption by the tissue of the fish. The trivalent is poorly absorbed (< 1%) across the intestinal wall (Dhanapal etal,1990)

2.3.b) EFFECT ON HUMAN

When chromium concentration exceeds a certain limit it becomes mutagenic.carcinogenic and tetrogenic (Balasubramanium etal,1996) Ingestion of Chromium(VI) may cause epigastric pain, vomiting, severe diarrhoea and haemorrage (Grover and Narayanaswamy 1982). Chromium is toxic to cause perforation, bronchiogenic carcinoma in continuously exposed humans (Varshney-1983).

2.3.c) EFFECT ON LAND

The presence of Chromium in the effluent also influences the metabolic activities of the plants resulting into reduced yields.

A pot experiment conducted with graded levels of chromium(VI) viz. 0,25,50,100,200,400,800, and 1000 mg/kg tannery sludge containg total 4 % chromium. Pollutant with rice IR 36 grown under flooded conditions using alluvial soil showed that in the dry season, the rice plant survived only up to 200 mg/kg (of chromium(VI)) sludge in the soil. Symptoms like leaf rolling and tip drying were also observed. Decrease in the grain and straw yield was also noted (Agarwal 1996)

2.4. DETOXIFICATION OF CHROMIU M (VI)

Detoxification of chromium may be done by i) by reduction and precipitation ii) ion exchange method .The first method is reliable but requires large settling tanks for precipitation of chromium hydroxides and subsequent sludge treatment.Ion exchange has the advantage of recovery of chromium(VI) but it is more expensive and sophisticated . (Alaerts, Jitjaturunt and Kelderman 1992).

REMOVAL OF CHROMIUM:- ADSORPTION TECHNIQUES

Recent studies on effluent treatment bearing chromium(VI) revealed adsorption on activated carbon as economically feasible alternative for small scale industries (Shrichand etal.,1994).

2.4.a) **ADSORPTION** is the accumulation of materials at an interface liquid, solid. Adsorption is used widely in wastewater treatment. Dissolved materials tend to either accumulate at interface depending on their relative strength of attraction for themselves or for the solvent (Donald Sundstorm 1979).

2.4.b) EFFECT OF ENVIRONMENTAL CONDITION ON ADSORPTION

Both the rate and extent of adsorption are affected by environmental conditions. A primary factor is pH.In general sorption capacity is increased by lowering of pH . Temperature also affects adsorption, adsorption equilibrium moves towards the sorptive phase with decrease in temperature (Edward P.Schroeder 1975)

2.4.c Many solids are used as adsorbents to remove impurities from fluids. Commercial adsorbent generally has a large surface area /unit mass.Common industrial adsorbents include silica gel, activated alumna molecular sieves.**Cr.(VI)** can be adsorbed by soil colloids including Fe and Al oxides.

(Robertson 1975,Davis and Leckie 1980 Benjamin and bloom 1981)

2.5. ADSORPTION ON ACTIVATED CARBON

Recently removal of chromium(VI) by means of adsorption on activated carbon has been developed into a promising alternative (Alaerts, Jitjaturunt and Kelderman 1992) Temperature of carbon activation affects the sorptive qualities of the materials. Since thermal activation yields a porous structure with large surface area .Weber noted that carbon activated near 400°C is a good acid adsorber. Other factors which influence the degree of chromium(VI) adsorption are found to be carbon dosage carbon particle size and Initial chromium(VI) concentration (Edward P.Schroeder 1975).

High cost and difficult procurement of activated carbon in India has prompted search for other suitable adsorbents.

2.5.a) **Flyash** a waste material from thermal power industries has been found to be a promising treatment for the removal of chromium(VI) (Grover, Narayanaswamy 1982)

2.5.b) A low cost adsorbent namely **GOAT HAIR** a waste material in the tanneries has been used to purify the effluent of the same tannery successfully with respect to eliminating the highly toxic chromium ions and found to be highly technical and economical method. (Balasubramanian 1996)

2.5.c) **THE USED TEA LEAVES** –a waste converted to carbonaceous material exhibits exceptionally high degree of chromium(VI) adsorption and hence can be utlised for the treatment of industrial waste water effluents containing chromium(VI) (Singh & Lal 1992) at an optimum pH $\cong 2$.

2.5.d) Through batch experiments, removal of chromium (VI) by **BLAST FURNACE FLUE DUST** generated in the steel plants has been studied, under ambient temperature and pH conditions removal effected to the extent more than 95 %

has been observed .The adsorption process follows I order kinetics with respect to metal ion concentration. (Patnaik & Das 1995).

2.5.e) **THE LEACHED ACACIAARABIC BARK** a waste material from vegetable tanning industries converted to a sorbent material by treatment with formaldehyde in acidic medium has exhibited a good sorption potential for Cr. (VI) with a peak value at pH2. (Singh, D.N.Saksena & Tiwari-1994).

2.5.f) Effective chromium removable from acidic electroplating waste water has been achieved by CSBAC. **COCONUT SHELL BASED ACTIVATED CARBON** .It is found that removal of chromium(VI) by CSBAC is almost complete (94%) after 4 hours of contact time, whereas 82% & 88% of chromium(VI) removal are observed after 20 minutes and one hour respectively at an optimum pH of 2.5 (Alaerts Etal-1989).

2.5.g) Removal of chromium from aqeous water has been investigated using adsorbents based on **BAGASSE AND COCONUT JUTE** and found to be in general most effective at low pH values (<2) The data for the adsorbents fit well to the Freundlich isotherm (Shri Chand, Agarwal & Pavankumar 1994).

Materials and Methods

3.MATERIALS AND METHODS

3.1 COLLECTION AND PRETREATMENT OF THE SAMPLE

In the present work removal of chromium (VI) from tannery effluent by adsorption technique has been studied.The activated saw dust carbon,activated bagasse carbon and raw saw dust were used as adsorbents.

The tannery effluent from an industry situated in ERODE has been selected for the present study. The sample was collected in 2.5 liter sterilized polythene containers. The pH of the sample was adjusted to pH2 using concentrated hydrochloric acid and stored in refrigerator at 4 °C.

Organic matters such as phenols present in the effluent though in tracer amounts will interfere in the determination and adsorption of chromium in the sample. Hence the sample has to be digested.

100 ml of the sample was digested with 10 ml of concentrated sulphuricacid, 2ml of hydrogenperoxide and 16 ml of concentrated nitric acid till the volume was

reduced to half and was made up of to the original volume.

3.2 REAGENTS

The following analytical grade regents had been used for the investigation

i)Concentrated nitric acid

ii)Concentrated sulphuric acid

iii)Liquor ammonia

iv)Potassium permanganate

v)Hydrogen peroxide 30 %

vi)Sodium azide

3.3 a)ADSORBENTS:

For the present studies raw saw dust activated saw dust carbon (**ASC**) and activated bagasse carbon (**ABC**) were used .The raw bagasse was collected from sugarcane juice shop and the raw saw dust from timber shop. The raw saw dust was used after washing with water and drying at 200° C for 5 hours .The dried material was ground and sieved through a 250 mesh.

3.3 b) PREPRATION OF ACTIVATED SAW DUST CARBON

One part (by weight) of raw saw dust was treated with one part by weight of concentrated sulphuricacid and kept at 150 °C in an oven for 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 carbon was ground and sieved through a 250 mesh.

3.3 c) PREPRATION OF BAGASSE CARBON

Four parts of raw bagasse was treated with three parts of concentrated sulphuric acid by weight and was kept in an oven 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 carbon was ground and sieved through a 250 mesh.

3.3 OXIDATION OF THE SAMPLE

The colorimetric method of determination of Chromium measures only hexavalent chromium. Also the presence of chromium (III) exerts a negative effect on activated carbon system. Trivalent chromium is not readily removable by the carbon, which only adsorbs bases.

Therefore in order to make activated carbon a feasible process for Chromium (VI) adsorption removal, some form of further treatment must be added to remove the Chromium (III) species. This can be done by oxidising the sample by strong oxidising agent like potassium permanganate prior to contact with carbon. (HUANG and BOWERS –1978)

10 ml of digested sample was pipetted out into a 250 ml beaker .Using methylorange as indicator added concentrated ammonia until the solution is just basic .then added 1:1 sulphuricacid dropwise until it was acidic and 1 ml in excess; after adjusting the volume to about 40 ml and it was heated to boiling. Potassium permanganate was added dropwise to maintain an excess of 2 drops. Boiled for two more minutes and then added sodium azide solution and continued boiling gently till

the colour had faded completely, Then cooled and added 0.25 ml of phosphoric acid.

3.3 BATCH EXPERIMENT:

To study the adsorbent capacities of the adsorbents batch experiments were carried out. Though industrial operations are not carried out batchwise these are simple and effective to evaluate the basic parameters affecting adsorption.

3.3 (a) EFFECT OF ADSORBENT DOSAGE

100 mL of samples containing 230 ppm of Chromium were contacted with adsorbents at a pH of 2. The system was equilibrated thoroughly on a horizontal bench shaker at room temperature for three hours. The weight of the adsorbent was varied from 100-1000 mg for ABC and for raw saw dust and 100-500 mg for ASC. After adsorption the suspension was filtered through a Whatman filter paper no.42. The filtrate was analysed colorimetrically (Digital systronics colorimeter 112) using filter No5 (540 nm) by complexing with diphenyl carbazide for residual Chromium (VI) concentration in the. solution.

3.3.(b) EFFECTS OF pH

The effect of pH was studied by varying pH from 1 to 5. The pH of the solution was adjusted by using dilute hydrochloricacid and sodium hydroxide and measured using Digital pentype pH meter (Henna). Varying amounts of adsorbents were taken depending upon their optimum dosage.

Results And Discussion

4.RESULTS AND DISCUSSION

Chromium is commonly contained in variety of industrial wastewaters, including those from the textile, leather tanning, electroplating and metal finishing industry. The effluents from these industries may contain toxic hexavalent chromium, in concentrations of some ten to few hundred mg/l. Chromium(V1)causes various genetic damages to DNA. Consumption of hexavalent Chromium at the rate of 10mg/kg of body weight leads to liver necrosis, nephritis and death (Roe 1977). Lower doses result in irritation of the gastro-intestinal mucous (Fregret and Rosman 1964). Chromium(V1)is toxic to aquatic animals and plants too. Higher concentration of chromium(V1) in water was reported to be lethal to various fishes. Although chromium exits in two oxidation states, namely +3 and +6, the biological fluid does not give any importance to the toxicity of chromium III. On animals chromium III is essential for metabolism.

Conventional means of removal of chromium(VI) include sulphide precipitation, hydroxide precipitation, flocculation,co-precipitation, ultra filtration, and solvent extraction. The application of activated carbon adsorption in water renovation has been well established.

In the present investigation locally available low cost adsorbents like raw saw dust, activated saw dust carbon and activated bagasse carbon were chosen as the adsorbents for chromium (VI) removal from tannery effluent.

EFFECTS OF ADSORBENT DOSAGE.

Experiments were conducted at room temperature and at pH2 with the same initial concentration of effluent 230ppm but with different weights of the above three adsorbents. The amount of adsorbent was varied from 100-1000mg for raw saw dust and bagasse carbon and 100-500mg for sawdust carbon.

Freundlich adsorption isotherm suggests linearity for the plot of log(x/m) against Ce. Tables 4,5,6 present the data of x,Ce, m and x/m. The Freundlich parameters K and l/n are indicators of adsorption capacity and intensity respectively. The values of K and l/n for the three systems are listed as below

TABLE - 4

pH: 2 Room temperature = 32°C. Adsorption of Cr(VI) on Activated Sawdust Carbon

Chromium(VI) initial concentration. (Co) PPM	Chromium(VI) absorbed(x) PPM.	Chromium (VI) equilibrium(Ce) PPM	Weight of ASC mg	Adsorption potential (%)	x/m	5 + log x/m	log Ce	m/x	1/ce
230	180	50	100	78	1.8	5.4550	1.6990	0.555	0.02
230	190	40	150	82. 6	1.27	5.1030	1.6020	0.789	0.025
230	198	32	200	86.1	0.99	5	1.505	1.01	0.033
230	205	25	250	89.1	0.82	4.913	1.397	1.219	0.04
230	210	20	300	91	0.7	4.8451	1.301	1.429	0.05
230	220	10	350	95	0.63	4.799	1	1.597	0.1
230	222	8	400	96.5	0.56	4.948	0.903	1.8	0.125
230	226	4	450	98.3	0.5	4.699	0.602	1.995	0.25
230	229	1	500	99.6	0.4600	4.662	0	2.183	0
230.0000	-	-	-	-	-	-	-	-	-

TABLE - 5

pH: 2 Room temperature = 32°C. Adsorption of Cr(VI) on Activated Bagasse Carbon

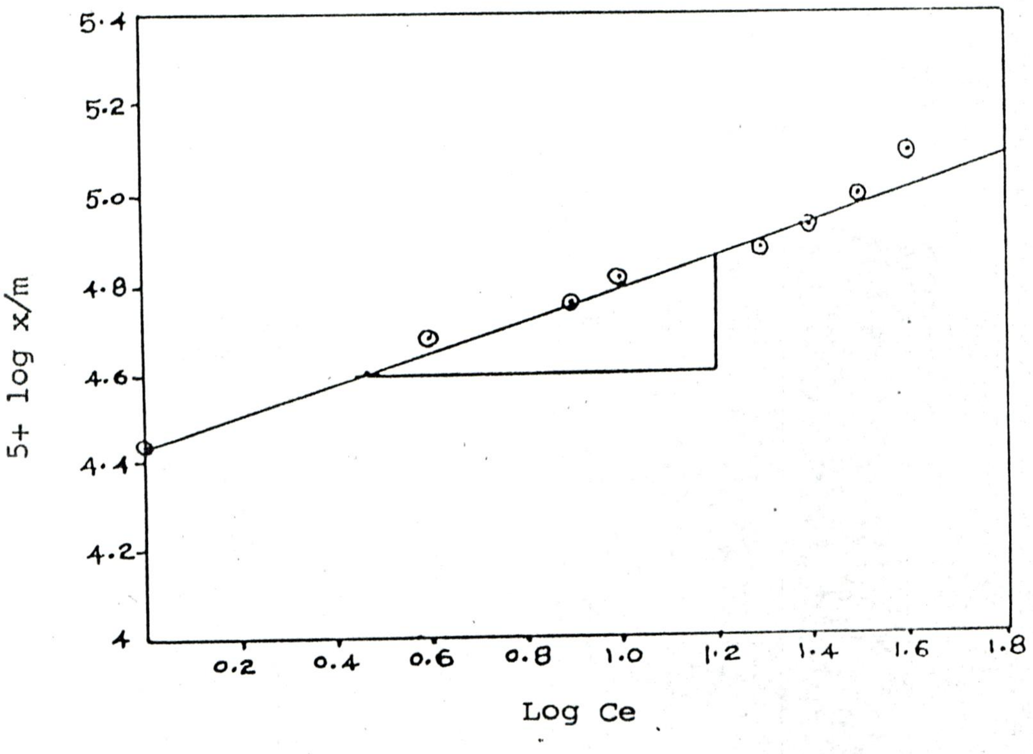
Chromium(VI) initial concentration. (Co) PPM	Chromium(VI) absorbed(x) PPM.	Chromium (VI) equilibrium(Ce) PPM	Weight of ASC mg	Adsorption potential (%)	x/m	5 + log x/m	log Ce	m/x	1/ce
230	160.0000	70	100	69.00	1.6	5.2042	1.8450	0.6250	0.0142
230	180	50	200	78.26	0.9	4.9542	1.6989	1.1111	0.0210
230	190	40	300	82.6	0.6	4.7979	1.6020	1.5789	0.0250
230	195	35	400	84.7	0.48	4.6812	1.5440	2.0513	0.0280
230	197	33	500	85.65	0.39	4.5910	1.5180	2.5300	0.0300
230	205	25	600	89.15	0.34	5.5328	1.3970	2.9260	0.0400
230	210	20	700	91.3	0.30	4.4777	1.3010	3.3330	0.0500
230	217	12.5	800	94.5	0.27	4.4314	1.0969	6.6780	0.0800
230	222	8	900	96.5	0.24	3.3802	0.9030	4.0540	0.1250
230	226	4	1000	98.00	0.23	4.3542	0.6020	4.4240	0.2500

TABLE - 6

pH: 2 Room temperature = 32°C. Adsorption of Cr(VI) on Raw Saw Dust

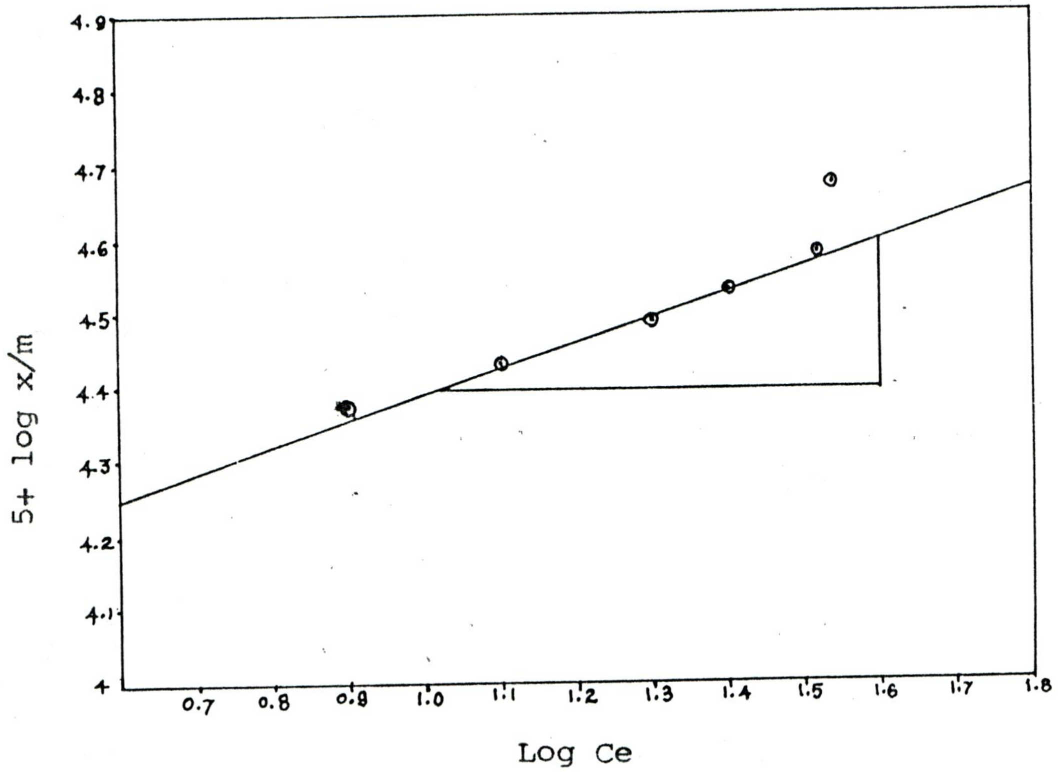
Chromium(VI) initial concentration. (Co) PPM	Chromium(VI) absorbed(x) PPM.	Chromium (VI) equilibrium(Ce) PPM	Weight of ASC mg	Adsorption potential (%)	x/m	5 + log x/m	log Ce	m/x	1/ce
230	62.5	167.5	100	27	0.625	4.7959	2.224	1.6	0.0059
230	70	160	200	304	0.35	4.5441	2.204	2.85	0.0062
230	90	140	300	39.13	0.3	4.4772	2.146	3.33	0.0071
230	110	120	400	48	0.275	4.4393	2.079	3.64	0.0083
230	130	100	500	57	0.26	4.4140	2.000	3.85	0.0092
230	150	80	600	65.2	0.25	4.3979	1.903	4	0.0125
230	170	60	700	73.9	0.24	4.3902	1.778	4.12	0.0166
230	190	40	800	82.6	0.237	4.3747	1.602	4.21	0.0250
230	204	26	900	88.7	0.227	4.3560	1.415	4.5	0.0380
230	212	18	1000	92.2	0.212	4.3260	1.255	4.72	0.0500

Fig.2 Freundlich Isotherm (ASC)



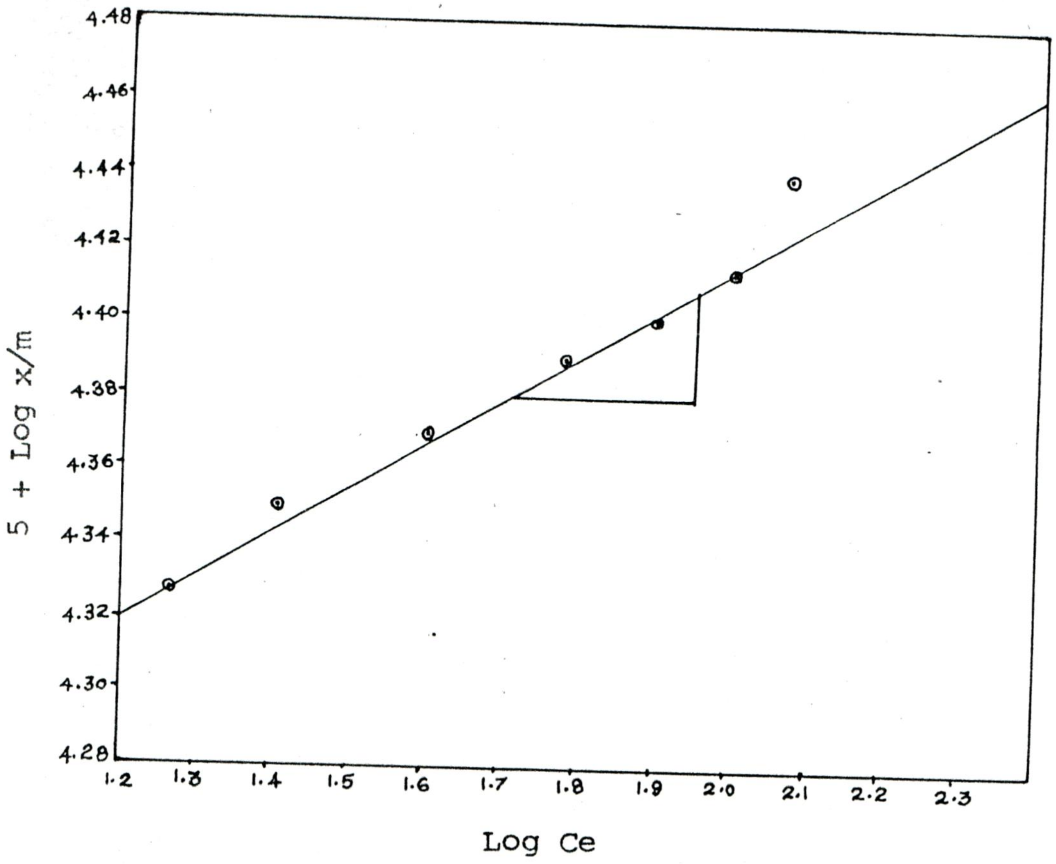
pH:2, Room Temperature 32 C, K=2512: 1/n=0.35
Initial concentration of Chromium (VI):230 ppm

Fig.3 Freundlich Isotherm (ABC)



pH:2, Room Temperature 32 C, K=316.2: 1/n=0.3509
Initial concentration of Chromium (VI):230 ppm

Fig.4 Freundlich Isothern(Raw Saw Dust)



pH:2,Room Temperature 32 C, K=2.399, 1/n=0.1273
Initial Concentration of Chromium (VI):230ppm

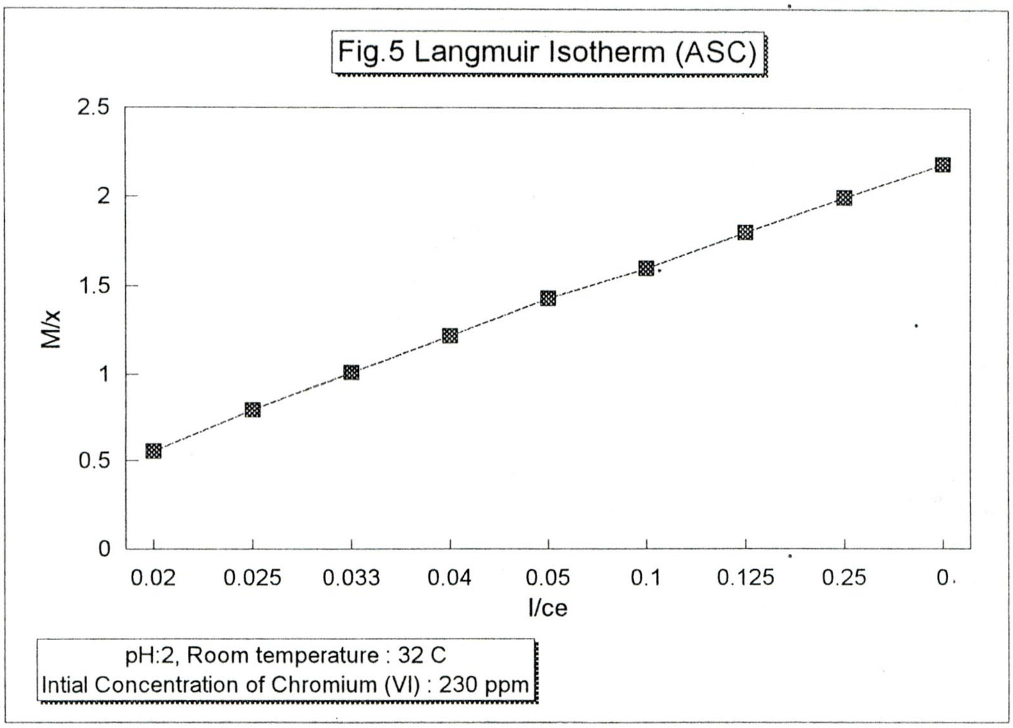


Fig.5 Langmuir Isotherm (ASC)

pH:2, Room temperature : 32 C
Intial Concentration of Chromium (VI) : 230 ppm

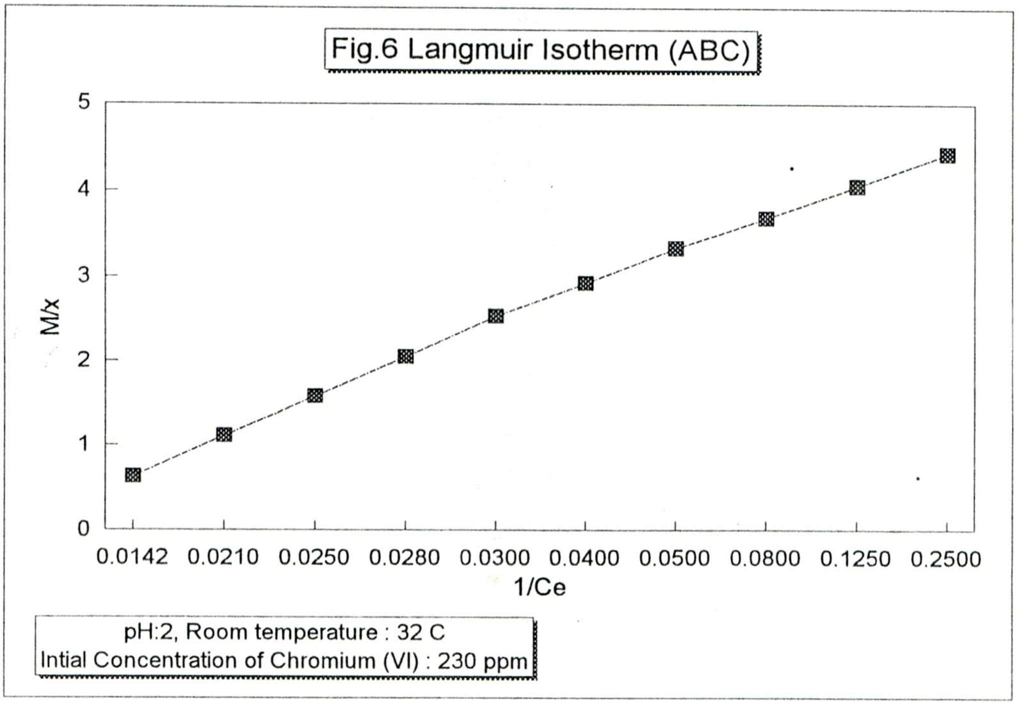
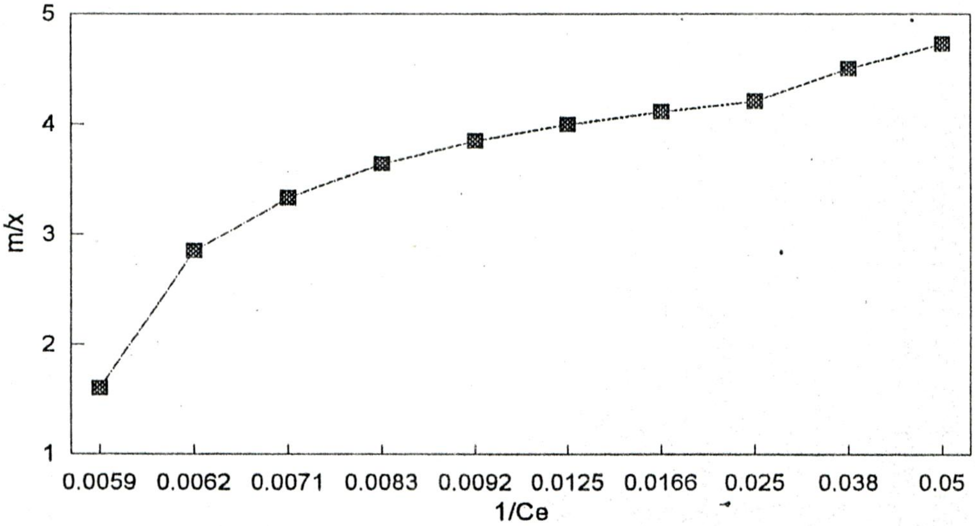


Fig.6 Langmuir Isotherm (ABC)

pH:2, Room temperature : 32 C
Intial Concentration of Chromium (VI) : 230 ppm

Fig.7 Langmuir Isotherm (Raw Saw Dust)



pH:2, Room temperature : 32°C
Intial Concentration of Chromium (VI) : 230 ppm

Values Of Freundlich Constants.

Absorbent	K	l/n
1. A S C	2512	0.35
2. A B C	316.2	0.3509
3. Sawdust	2.399	0.1273.

Since l/n is less than one, it indicates favourable adsorption. The K value shows that the adsorption capacities are in the order ASC > ABC > Raw Sawdust.

The chromium (VI) interaction with activated carbon is a complicated phenomenon. Two mechanisms are recognized in the removal of chromium (VI) by the activated carbon. The reduction reaction which reduces chromium (VI) to chromium (III) and adsorption reaction which results in the attachment of mainly chromium (VI) species and to a lesser extent the chromium (III) species. A hydrolytic surface reaction resulting in a drastic increase in solution pH is also taking place when carbon is brought into contact with water. (Haung and Bowers- 1977).

During the first stage of removal reduction dominates the interfacial reaction. The chromium (VI) rate then gradually slows down as the H+ ions are used up for hydrolysis and an equilibrium concentration of chromium (III) is reached. The latter stage of chromium (VI) removal is mainly due to the adsorption of the chromium (VI) species.

The reduction of chromium (VI) exerts a negative effect on an activated carbon system. The trivalent chromium is not readily removable by the activated carbon which only adsorbs bases. The mechanism of reaction may be represented as,

$$\mathbf{CrO_4^{2-} + 8H^+ + 8e^- \qquad 2Cr^{3+} + 4H_2O}$$

This reaction causes a significant increase in solution pH and thereby slows down the chromium (VI) adsorption. Therefore in order to make the chromium adsorption feasible either the carbon must be given pretreatment or the effluent must be oxidised with strong oxidising agents like potassium permanganate which stabilizes the chromium (VI) species in the solution which suppresses the reduction of chromium (VI) to chromium III.(Haung and Bowers –1977)

In the present work the effluent was oxidised with potassium permanganate to suppress the reduction of chromium (VI) to chromium (III). Also in the present study the pH of the solution after reaction remained unchanged revealing that chromium (VI) removal proceeds mainly via the adsorption mechanism.

Effect of pH on Adsorption of Chromium: -

To study the effect of pH, experiments were conducted by varying the pH from 1 to 5 for all the three adsorbents. The initial concentration of the chromium (VI) had been kept constant (230ppm). The results suggested at below pH 3 adsorption was maximum for all the 3 adsorbents at their optimum dosage.(ASC=300mg/100 ml;ABC=600mg/100 ml;Raw saw dust =800mg/100 ml) But at higher pH the adsorption was found to be decreased.

The optimum pH for the adsorption of chromium (VI) had been chosen as 2 for all the three absorbents at their optimum dosage.

Improved adsorption at low pH may be explained on the assumption that the activated carbon consists of active sites bearing negative charge which are neutralized by H+ ions thereby reducing hindrance to diffusion of chromium (VI) ions. Reduction in adsorption at higher pH is possibly

TABLE-7

EFFECT OF pH ON ASC

Weight of ASC:300mg/100 ml Room temperature=32°C

Chromium(vi)initial concentration Co ppm	Chromium(VI) adsorbed x ppm	Chromium (VI) equlibrium Ce Ppm	p H of the solution	Adsorption potential %
230	223	7	1	96.9
230	211	19	2	91.7
230	147.5	82.5	3	64.3
230	125	105	4	54
230	115	115	5	50

TABLE-8

EFFECT OF pH ON ABC

Weight of ABC=600mg/100 ml **Room temperature=32°C**

Chromium (VI)initial concentration Co ppm	*Chromium (VI)adsorbed x ppm*	*Chromium (VI) equilibrium Ce ppm*	*pH of the solution*	*Adsorbtion potential %*
230	229	1	1	99.5
230	205	25	2	89.13
230	153	77	3	66.5
230	130	100	4	56
230	110	120	5	47.8

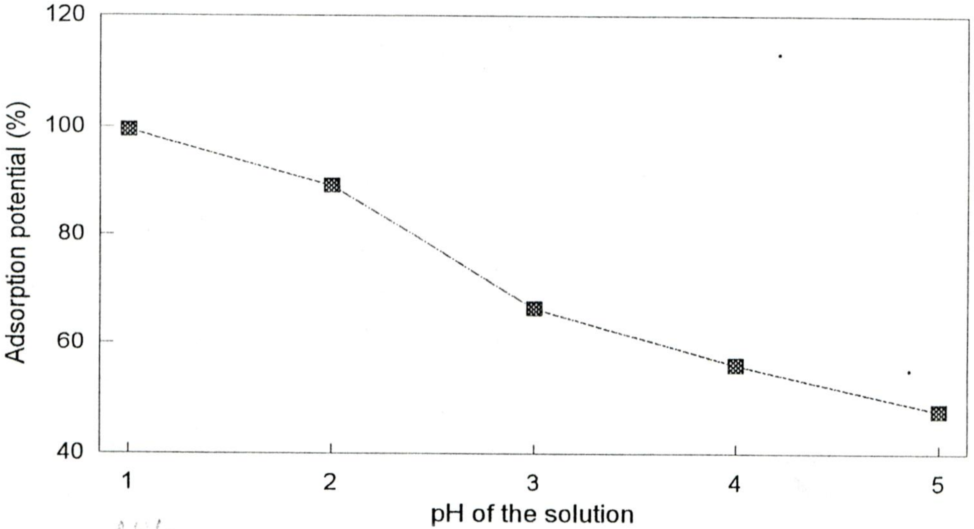
TABLE-9

EFFECT OF pH ON RAW SAW DUST

Weight of saw dust=800mg/100 ml Room temperature=32°C

Chromium (VI) initial concentration Co ppm	*Chromium (VI) adsorbed x ppm*	*Chromium (VI)EQulibrium Ce ppm*	*pH of the solution*	*Adsorption potential %*
230	225	5	1	97.8
230	204	26	2	88.7
230	175	55	3	76
230	120	110	4	52
230	100	130	5	43

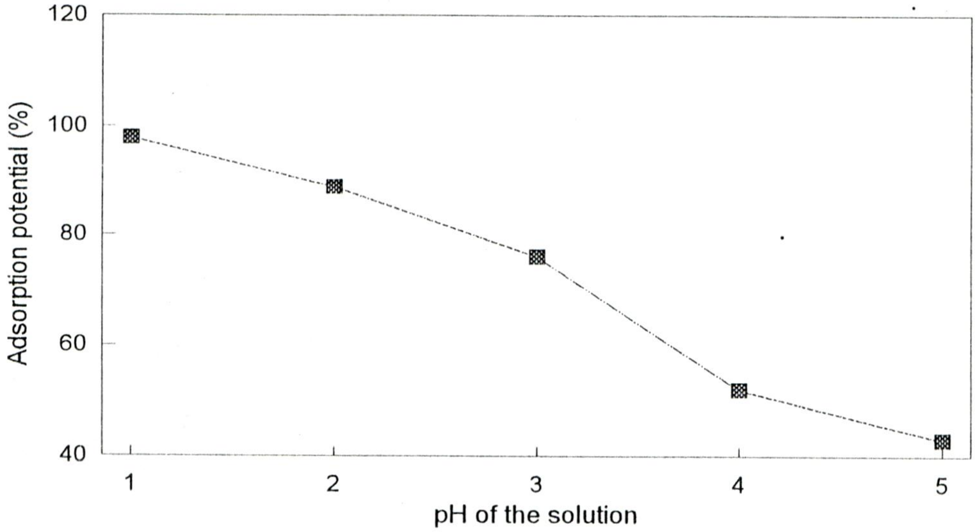
Fig. 9 Effect of pH on ABC



ABC

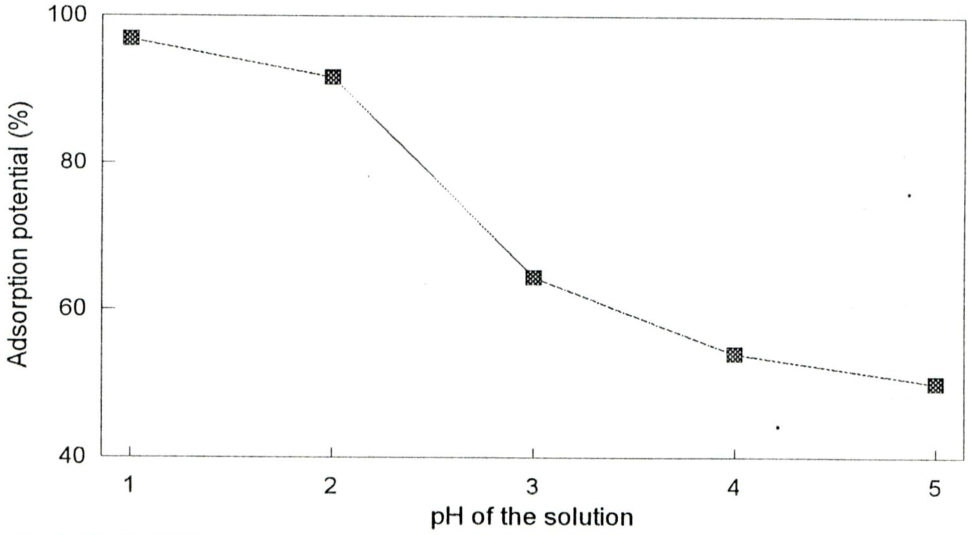
Weight of ASC = 300 mg/100ml, Room temperature = 32 C
Intial Concentration of Chromium (VI) = 230 ppm

Fig.10 Effect of pH on Raw Saw Dust



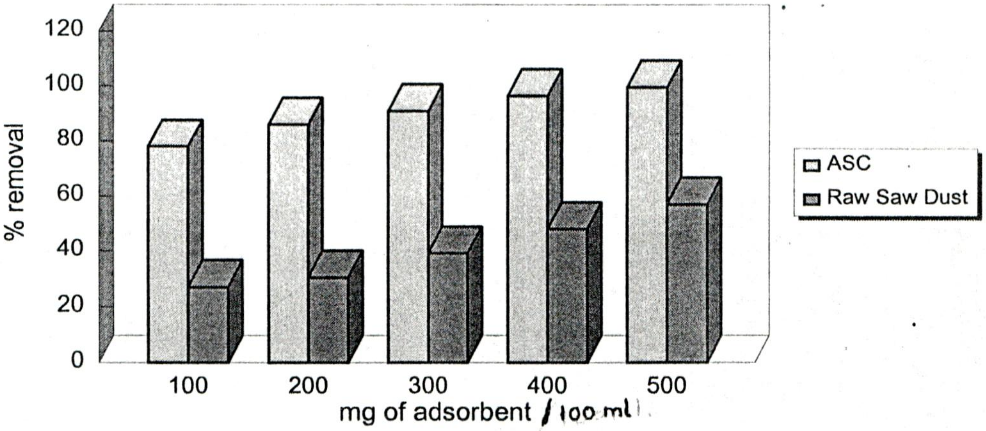
Weight of Raw Saw Dust= 800 mg/100ml, Room temperature = 32 C
Intial Concentration of Chromium (VI) = 230 ppm

Fig. 8 Effect of pH on ASC



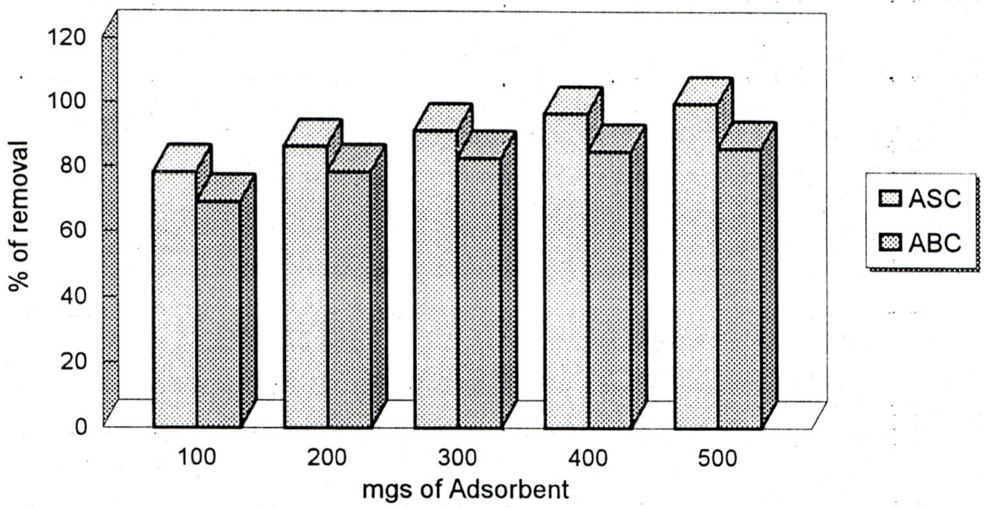
Weight of ASC = 300 mg/100ml, Room temperature = 32 C
Intial Concentration of Chromium (VI) = 230 ppm

Fig. 12 COMPARISION OF ABDSORPTION POTENTIALS OF ASC & RAW SAW DUST



Room temperature = 32 C, pH of the solution :2
Initial Conc. of Cr (vi) = 230 ppm

Fig. 11 COMPARISION OF ADSORPTION POTENTIAL OF ASC AND ABC



Room temperature = 32 C, pH of the solution :2
Initial Conc. of Cr (vi) = 230 ppm

due to increased solubility of chromium(VI) and the abundance of OH^- ions thereby increasing hindrance to diffusion of chromium (VI) ions.(Grover and Narayanaswamy - 1982)

Summary and Conclusion

5. SUMMARY AND CONCLUSION

In the present work the adsorption of chromium (VI) on three-adsorbents viz. Raw Sawdust, activated sawdust carbon and activated bagasse carbon were studied.

The findings of the studies reveal that, effective chromium(VI) removal from tannery effluent can be achieved by activated carbon. The activated saw dust carbon exhibited higher capacity in the removal of chromium (VI) from the tannery effluent. The order of adsorption for the three adsorbents is as follows,

ASC > ABC > Raw sawdust.

On increasing the dosage of adsorbents the adsorption increases upto certain extent but on further increase in adsorbent dosage,the adsorption remains constant, as per Langmuir adsorption studies. The adsorption also obeyed Freundlich isotherm.

The maximum adsorption of chromium (VI) can be achieved by maintaining pH below three at their optimum dosage.[ASC=300mg/100ml;ABC=600mg/100ml;Raw saw dust=800mg/100ml.

To have maximum adsorption of chromium (VI) the effluent must be oxidized prior to adsorption which stabilize the chromium (VI) ions in solution.

Conditions to be maintained for maximum chromium (VI) adsorption are,

i)The effluent must be oxidised with very strong oxidising agent like $KmnO_4$

ii)The pH of the solution must be maintained at≅2.

Hence from the studies we conclude that for chromium (VI) adsorption activated carbon from saw dust a low cost adsorbent can be effectively used at optimum pH of 2 for the removal of chromium (VI) from tannery effluent. Also the effluent must be oxidised with strong oxdising agents such as potassium permanganate to achieve maximum adsorption.

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Appendices

5. APPENDIX.

Estimation of chromium [colorimetric method]
Principle: -

Under acidic conditions hexavalent chromium reacts with s-diphenyl carbazide to form a reddish violet coloured complex which can be determined colorimetrically.

Regents: -

Double distilled water was used for the preparation of reagents.

a) Stock chromium solution: 41.4mg of potassium dichromate solution was dissolved in water and diluted to 100ml. {1ml = 50.0mg of chromium}

b) Standard chromium solution: 10ml of stock chromium solution was diluted to 100ml. 1.00ml = 5.00mg of chromium.

c) O.2N sulphuric acid: 8ml of concentrated sulphuric acid were diluted to 1 litre with water.

d) Diphenyl carbazide solution: 250mg of s-diphenyl carbazide was dissolved in acetone and made upto 50ml. Stored in brown bottle.

Procedure:

Preparation of calibration curve:

To compensate for possible slight losses of chromium during digestion or other analytical operation chromium standards were treated as samples.

Accordingly measured volumes of standard solution (1ml = 5mg of chromium) ranging from 5 to 20 ml to give standards of 25 to 100mg of chromium,were pipetted out in 100-ml standard flask. To these solutions 1ml of 0.2N H_2SO_4 were added and made up to 100 ml. And added 2 ml of diphenyl carbazide solution to each of these solutions. After 15 minutes the violet colour developed was read at 540mm. Using the reagent blank absorbance was corrected to zero.

The above procedure was repeated for sample also. From the corrected absorbence chromium in the sample was determined with reference to the calibration curve.