Anand Charitable Sanstha Ashti's

ANANDRAO DHONDE ALIAS BABAJI MAHAVIDYALAYA, KADA

TAL. ASHTI, DIST. BEED (MS) - 414 202

Phone - 02441-239621, 239921 Fax No. 02441-239621

E-mail. : admkada@gmail.com Website : www.admkada.com Principal Dr. H.G. Vidhate

Ref. No.: Admk / 2020-2021/ 56

Date: 09/10 / 2020

To,
The Deputy Registrar,
Planning and Statistical Section
Dr. B. A. M. University,
Aurangabad.

Subject: - Submission of the Final report of Minor research Project with Utilization Certificate and Expenditure Statement……
Ref. No.: - *STAT/VI/RG/Dept/2018-19 Date: -31/01/2019.*

Respected Sir,

With reference to above cited subject. I have pleasure to mention that **Dr. D. B. Jirekar** is working in our college as Assistant professor in Chemistry. Dr. B. A. M. University, Aurangabad sanctioned him a minor research project with grant amount **Rs.** ***35000/-*** (*Thirty-five thousand rupees only*) entitled ***"Study of Adsorption Capacity of Low-Cost Bio-materials for the removal of Hazardous Chemicals".***

O/C

The principal investigator has completed this project in time but because of COVID 19, we couldn't submit it in time. He has received out granted amount only **Rs.** ***17500/-*** (*Seventeen thousand five hundred rupees only*) as a first instalment, please credit his remaining amount and accept final report with utilization certificate and expenditure details.

Thanking you,

Covid-19 मुळे जमा करण्यास उशीर झाला

13/10/2020

Plan & Stat
Inward No. 83
Date 13/10/2020

Principal
Anandrao Dhonde Alias Babaji College
Kada, Tal. Ashti, Dist. Beed
Mob. 7507085901

Encl.

1) Utilization Certificate and Statement of Expenditure.
2) Final report of Minor research Project.

Final Report of Minor Research Project

"Study of Adsorption Capacity of Low-Cost Bio-materials for the removal of Hazardous Chemicals"

Planning and Statistical Section

Dr. Babasaheb Ambedkar Marathwada University, Aurangabad.

Submission Final Report of Minor Research Project

In

Chemistry

Under the area of Inorganic and Physical Chemistry

Principal Investigator

Dr. Jirekar Dattatraya Babasaheb

(Head, Dept. of Chemistry)

Anand Charitable Sanstha Ashti's
Anandrao Dhonde Alias Babaji Mahavidyalaya, Kada
Tal. Ashti, Dist. Beed. 414202.

Ref: No. – STAT/VI/RG/Dept/2018-19 Date: -31/01/2019

March - 2020

Dr. Babasaheb Ambedkar Marathwada University, Aurangabad

STATEMENT OF EXPENDITURE I N RESPECT OF MINOR RESEARCH PROJECT

Letter Ref: No. – STAT/VI/RG/Dept/2018-19 Date: -31/01/2019

Name of Principal Investigator: ***Dr. Jirekar Dattatraya Babasaheb.***

Dept. of Chemistry. Anandrao Dhonde Alias Babaji Mahavidyalya, Kada. Tq. Ashti. Dist. Beed. - 414202.

FIRST INSTALMENT RECEIVED AMOUNT – ***Rs. 17,500/-***

EXPENDITURE OF TOTAL AMOUNT – ***Rs.*** **41,058.71 /-**

1. BOOKS:

Sr. No.	Date	Title	Author	Qty.	Amount (Rs.)
1	10.03.2020	Kinetics of metal Ions Adsorption from Aqueous Solutions	Sotira Yiacomi Chi Tien	01	5,629.71
2	10.03.2020	Surface Chemistry Essentials	Cloudtall	01	2,290.00
3	10.30.2020	Little Adsorption Book	Diran Basmadjian	01	1,589.00
Total Rupees: *Nine thousand five hundred eight rupees & seventy-one Paise*					**9,508.71**

2. *CHEMICALS:*

Sr. No.	Date	Particular/on account of	Remarks	Amount
1	12.04.2019	Chemicals	Chemicals for project work	1526.00
2	12.04.2019	Chemicals	Chemicals for project work	1640.00
3	13.04.2019	Chemicals	Chemicals for project work	1761.00
4	13.04.2019	Chemicals	Chemicals for project work	1373.00
5	27.06.2019	Chemicals	Chemicals for project work	1995.00
6	12.07.2019	Glassware	Glassware for project work	1950.00
7	13.08.2019	Glassware's	Glassware's for project work	1896.00
8	20.08.2019	Chemicals and Glassware's	Chemicals and Glassware's for project work	1900.00
Total Rupees: *Fourteen thousand forty-one*				**14041.00**

3. CONTINGENCY:

Sr. No.	**Date**	**Particular/on account of**	**Remarks**	**Amount**
1	07.03.2019	Xerox and Computer print	Xerox of materials and Research papers for project work	855.00
2	10.03.2019	Conference Registration fee	ACTRA, Aurangabad.	900.00
3	12.04.2019	Stationary	Marking pen, File, Registers. etc.	1204.00
4	21.09.2019	Conference Registration fee	Gandhi College, Kada.	700.00
5	05.11.2019	Paper publication Charges	International Journal of Chemical Science	1000.00
6	29.12.2019	Stationary	Register and graph papers	310.00
7	29.12.2019	Stationary	Box file and stapler pin box	411.00
8	08.02.20120	Conference Registration fee	ACTRA, Aurangabad.	600.00
9	19.03.2020	Computer typing of Final Research project	Final Research project work	2000.00
10	20.03.2020	Comp. Print (colour) with Xerox of Final Research project	Expenditure statement of Research project work	2000.00
11	21.03.2020	Paper publication Charges	International Research Journal of Modernization in Engineering technology and Sciences.	499.00
12	25.03.2020	Xerox and Binding	Five copies of Final Research project work	2000.00
13	31.03.2020	Paper publication Charges	Research paper published in Inter. Jour. Of Innovations Engineering & Technology	1000.00
Total Rupees: *Thirteen thousand four hundred seventy-nine only*				**13,479.00**

4. TRAVELING AND FIELD WORK:

Sr. No.	Date	Particular/on account of	Remarks	Amount
1	08.02.2019	Travelling Aurangabad	Submission of acceptance of minor research project work	460.00
			D.A.	120.00
2	07.03.2019	Travelling Aurangabad	Submission of Requestion for an advance for project work	460.00
			D.A.	120.00
3	10.03.2019	Travelling, Aurangabad	Traveling for attending National seminar.	460.00
4	12.04.2019	Travelling Ahmednagar	Purchase Chemical's for project work	170.00
5	13.04.2019	Travelling, Ahmednagar	Purchase Chemical's for project work	170.00
6	27.06.2019	Travelling, Ahmednagar	Purchase Chemical's for project work	170.00
7	12.07.2019	Travelling, Ahmednagar	Purchase Glassware's for project work	170.00
8	13.08.2019	Travelling, Ahmednagar	Purchase Glassware's for project work	170.00
9	20.08.2019	Travelling, Ahmednagar	Purchase Chemical's for project work	170.00
10	21.09.2019	Travelling, Aurangabad	Traveling for attending National seminar.	460.00
11	26.03.2020	Travelling	Travelling for taking signature of C/A	350.00
12	30.03.2020	Travelling Aurangabad	Submission of minor research project work	460.00
			D.A.	120.00
Total Rupees: *Four thousand thirty only*				**4,030.00**

Certified that the above expenditure is in accordance with Dr. BAMU, Aurangabad norms for Minor Research Projects

Principal Investigator

Principal

PRINCIPAL
Anandrao Dhonde Alias Babaji
College, Kada, Tal. Ashti, Dist. Beed

ACCESSION CERTIFICATE

It is certified that the Books purchased from **Minor Research Project** grants **Dr. Jirekar Dattatraya Babasaheb** handed over to the College library. Their accession number are from to

Books Purchased From Minor Research Project

Sr. No.	Accession No	Title of the Books	Author	Qty.	Amount (Rs.)
1	**18643**	Surface Chemistry Essentials	Cloudtall	01	2,290.00
2	**18644**	Little Adsorption Book	Diran Basmadjian	01	1,589.00
3	**18645**	Kinetics of metal Ions Adsorption from Aqueous Solutions	Sotira Yiacomi Chi Tien	01	5,629.71
				03	**9,508.71**
Total Rupees: Nine thousand five hundred eight rupees & seventy one Paise					**9,508.71**

Principal Investigator

Librarian

31.7.2020.

Principal

PRINCIPAL
Anandrao Dhonde Alias Babaji
College, Kada, Tal. Ashti, Dist. Beed

Annexure - III

Dr. Babasaheb Ambedkar Marathwada University, Aurangabad.

Final Report of the work done on the Minor Research Project

1. Project report No. : ***Final Report***
2. Letter Reference : **Ref: No. – STAT/VI/RG/Dept/2018-19**

   Date: -31/01/2019
3. Period of report: from : ***31/01 / 2019 to 31 /03 /2020***
4. Title of research project: ***"Study of Adsorption Capacity of Low-Cost Bio-materials for the removal of Hazardous Chemicals".***
5. (a) Name of the Principal Investigator: - ***Dr. Jirekar Dattatraya Babasaheb.***

   (b) Dept. and University/College where work has progressed: - ***Dept. of Chemistry.***

   Anandrao Dhonde Alias Babaji Mahavidyalya, Kada.

   Tq. Ashti. Dist. Beed (M.S.) - 414202.
6. Effective date of starting of the project: - **31 /01 / 2020**
7. Grant approved and expenditure incurred during the period of the report:

   a. Total amount approved Rs.**: 35,000**/- *(Thirty-five thousand only.)*

   b. Total amount received Rs**. : 17,500/-** *(Seventeen thousands five hundred only.)*

   c. Total expenditure Rs. **: 41,058.71**/- (*Forty one thousand fifty eight rupees and seventy-one paise)*

Report of the Work Done

1. Brief objective of the project: ***The aim of the present work is to study the removal of hazardous metal ions and organic materials adsorption technique using leaves of Sarpgandha agricultural low-cost materials. The main advantage of agricultural low-cost materials is that they are very cheap, easily available in excess quantities eco-friendly and hence can be used to remove hazardous heavy metal ions and organic materials from water.***

Annexure - III

2. Work done so far and results achieved and publications, if any, resulting from the work (Give details of the papers and names of the journals in which it has been published or accepted for publication: - *03* – ***Research papers are Published and 02 are communicated.***
3. Has the progress been according to original plan of work and towards achieving the objective? If not, state reasons: --
4. Please indicate the difficulties, if any, experienced in implementing the project: **No.**
5. If project has not been completed, please indicate the approximate time by which it is likely to be completed. A summary of the work done for the period (Annual basis) may please be sent to the Commission on a separate sheet: ***Project is completed.***
6. If the project has been completed, please enclose a summary of the findings of the study. Two bound copies of the final report of work done may also be sent to the Commission: ***Project is completed.***
7. Any other information which would help in evaluation of work done on the project. At the completion of the project, the first report should indicate the output, such as (a) Manpower trained (b) Ph. D. awarded (c) Publication of results (d) other impact, if any

Manpower trained and this work is useful for the graduate level students, about information of the removal of hazardous metal ions and organic materials adsorption technique using different agricultural low-cost materials. This work is also useful for the newly researchers as well as ph. D. students.

Principal Investigator

Annexure - IV

Dr. Babasaheb Ambedkar Marathwada University, Aurangabad.

Utilization certificate

Certified that the grant of Rs. **17, 500/-** (Seventeen *thousand five hundred rupees only*) received from the Dr. Babasaheb Ambedkar Marathwada University, Aurangabad under the scheme of support for Minor Research Project entitled *"Study of Adsorption Capacity of Low-Cost Bio- materials for the removal of Hazardous Chemicals"*. Vide Dr. BAMU, Aurangabad letter Ref: No. – STAT/VI/RG/ Dept/2018-19 Date:-31/01/2019 have been **41,058.71**/- (*Forty one thousand fifty eight rupees and seventy one paise)* utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission.

Principal Investigator

K. N. Kotecha

Statutory Auditor

KALYAN N. KOTECHA
KOTECHA & CO.
CHARTERED ACCOUNTANTS
M.No.011386
BEED.

Principal

PRINCIPAL
Anandrao Dhonde Alias Babaji College
Kada, Tal. Ashti, Dist. Beed

Annexure - V

Dr. Babasaheb Ambedkar Marathwada University, Aurangabad.

STATEMENT OF EXPENDITURE I N RESPECT OF MINOR RESEARCH PROJECT

1. Name of Principal Investigator: ***DR. JIREKAR DATTATRAYA BABASAHEB.***

2. Dept. of College : ***Dept. of Chemistry. Anandrao Dhonde Alias Babaji Mahavidyalya, Kada. Tq. Ashti. Dist. Beed. - 414202.***

3. Letter Reference No. and Date: **Ref: No. STAT/VI/RG/Dept/2018-19**

Date: - 31/01/2019

4. Title of the Research Project : ***"Study of Adsorption Capacity of Low-Cost Bio-materials for the removal of Hazardous Chemicals".***

5. Effective date of starting the project: ***01/03 / 2019.***

6. a. Period of Expenditure: ***From 01 /03 / 2019 to 31 / 03 /2020.***

b. Details of Expenditure:

Sr. No.	Items	Total Expenditure Amount (Rs.)
i	**Books & Journals**	***9,508.71***
ii	**Chemicals and glassware**	***14,041.00***
iii	**Contingency**	***13,479.00***
iii	**Field Work / Travel.**	***4,030.00***
Total Rupees*: Forty-one thousand fifty-eight rupees and seventy one paise*		**41,058.71**

Annexure - V

It is certified that the grant of Rs. **17,500/-** (Seventeen *thousand five hundred rupees only*) received from the Dr. Babasaheb Ambedkar Marathwada University; Aurangabad under the scheme of support for Minor Research Project entitled *"Study of Adsorption Capacity of Low-Cost Bio- materials for the removal of Hazardous Chemicals"*. Vide Dr. BAMU, Aurangabad letter Ref: No. – STAT/VI/RG/Dept/2018-19 Date: -31/01/2019 **have** been 41,058.71/- (*Forty-one thousand* **fifty-eight** *rupees and seventy-one paise)* utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission.

Principal Investigator

Principal

PRINCIPAL
Anandrao Dhonde Alias Babaji
College, Kada, Tal. Ashti, Dist. Beed

Final Report of Minor Research Project

"Study of Adsorption Capacity of Low-Cost Bio-materials for the removal of Hazardous Chemicals"

Planning and Statistical Section

Dr. Babasaheb Ambedkar Marathwada University, Aurangabad.

Submission Final Report of Minor Research Project

In

Chemistry

Under the area of Inorganic and Physical Chemistry

Principal Investigator

Dr. Jirekar Dattatraya Babasaheb
(Head, Dept. of Chemistry)

Anand Charitable Sanstha Ashti's
Anandrao Dhonde Alias Babaji Mahavidyalaya, Kada
Tal. Ashti, Dist. Beed. 414202.

Ref: No. – STAT/VI/RG/Dept/2018-19 Date:-31/01/2019

March - 2020

ACKNOWLEDGMENT

It will start with my God who gave me the life, strength and the perseverance, who equipped me with the right tools to study science. It gives me great pleasure to express my sincere thanks and deep sense of indebtedness to my ***Principal Dr. H. G. Vidhate,*** *Anandrao Dhonde Alias Babaji Mahavidyalaya, Kada. and Management Council Member, Dr. B. A. M. University, Aurangabad for his motivation, co-operation and encouragement during my project work.*

My sincere thank,s to ***Shri Bhimraoji Dhonde*** *Secretory, Anand Charitable Sanstha, Ashti. Dist- Beed. for their kind encouragement and inspiration during research work.*

I would like to extend my sincere thanks to ***Principal Dr. Mazahar Farooqui,*** *Maulana Azad College, Aurangabad, who took me on as a student and pushed and pulled me forward from day one. The constructive criticism, inspiration, affection, keen interest and critical evaluation of the project work of my guide are the motivating force behind this endeavor. His insights patience and superb knowledge of laboratory procedures, pertinent literature, and how to phrase scientific documents have been invaluable for the completion of this project.*

I express thanks to my Colleague Dr. Smt. P. P Ghumare, Mr. I. G. Nannaware, Dr. B. N. Gawade and Mr. Ajinath Suryawanshi for their co-operation in my research work.

I am also grateful to my friends Dr. D. S. Bodkhe, Dr. B. S. Khaire, Dr. G. M. Pathare, Dr. R. G. Vidhate, Dr. S. D. Gaikwad, Dr. Smt. G. S. Jagtap, who made my life happy with their company and support during the period of my research work.

I will be failing in my duties, if I won't express my heartfelt thanks to my family members, Mrs. SavitaJirekar (wife), Dhairyashil and Dhananjay (son) for being a constant source of inspiration for me. Without their love, understanding, affection, support and praise this work would not have been completed. At last but not least I would like to thank all those who helped me in completing this project work directly or indirectly.

Dr. Jirekar Dattatraya Babasaheb
(Head, Dept. of Chemistry)

CERTIFICATE

This is to certify that Dr. Jirekar Dattatraya Babasaheb has satisfactory completed his minor research project in entitled "Study of Adsorption Capacity of Low-Cost Bio-materials for the removal of Hazardous Chemicals" is in the subject of Chemistry as laid down in the regulation of Dr. Babasaheb Ambedkar Marathwada University, Aurangabad during the academic year march-2019-2020.

Place: Kada

Date: 23/03/2020

Principal

PRINCIPAL
Anandrao Dhonde Alias Babaji
College, Kada, Tal. Ashti, Dist. Beed

INDEX

ABBREVIATIONS

Sr. No.	Particulars	Abbreviations
1	Congo Red	CR
2	Methylene Blue	MB
3	Chromium metal ion	Cr (VI)
4	Copper metal ion	Cu (II)
5	Initial concentration	C_0
6	The equilibrium concentration (mg/L)	C_e
7	Energy of adsorption	b
8	Separation factor	R_L
9	Adsorption capacity	k_f
10	Equilibrium rate constants	K_c
11	Langmuir constants related to capacity of adsorption (mg/g)	Q_0
13	The amount of adsorbate adsorbed (mg/g) at equilibrium time	q_e
14	The amount of adsorbate adsorbed (mg/gm) at time t	q_t
15	The first order rate constant (min^{-1})	K_1
16	The second order rate constant ($gm.mg^{-1}.min^{-1}$)	K_2
17	Kelvin	k
18	Gram	g
19	Minute	min
20	Gibb’s free energy change	ΔG^0
21	Enthalpy change	ΔH^0
22	Entropy change	ΔS^0
23	Concentration	Conc.
24	Sarpgandh Leaves Powder	SLP

Study of Adsorption Capacity of Low-Cost Bio-Materials for the Removal of Hazardous Chemicals

1. Introduction

1.1.Introduction:

“Water is the hub of life" water is an important and life sustaining drinks to humans and is essential to the survival of all organisms [1]. Many places water availability is falling to crisis levels more than 80 countries, 40% of the world's population are already facing water shortages by the year 2020, the world population will double. The cost of water, infra-structure has risen dramatically. In the 21st century environmental pollution is one of the major threats to human life. Among the different types of pollution, waste water stream is one of the major problems due to the fact that large amount of water used in our daily life. Waste water quality can be defined by physical, chemical or biological characteristics; waste water generally contains toxic inorganic and organic pollutants. Inorganic pollutants consist of mineral acids, inorganic salts, finely divided metal compounds, trace elements, cyanides, nutrients, and organometallic compounds. There are several classes of water pollutants. The first category includes disease causing agents like bacteria, viruses, protozoa and parasitic worms that enter sewage systems and untreated waste. The second category of water pollutants is oxygen demanding wastes, wastes that can be decomposed by oxygen requiring bacteria, when large populations of decomposing bacteria are converting these wastes it can deplete oxygen levels in the water. This causes other organisms in the water such as fish, algae, fungi etc. to die. The third class of water pollutants is water soluble inorganic pollutants such as acids, salts, and toxic metals. Large quantities of these compounds make water unfit to drink and cause the death of life. Another class of water pollutant is nutrients; they are water soluble nitrates and phosphates that cause excessive growth of algae and other water plants which deplete the water's oxygen supply. It kills fish. If it finds in drinking water, it is fatal to children.

The introduction of waste products in the environment is a worldwide problem that has been highlighted by various environmentalist groups. Colored organic effluent is produced in industries such as textile, oil, rubber, paper, plastic pesticides cosmetics etc. Discharging of dyes into water resources even in a small amount can affect the aquatic life and food web. Dyes can also cause allergic dermatitis and skin irritation some of them have been reported to be carcinogenic and mutagenic for aquatic organisms [2].

Finally, water soluble radioactive compounds cause diseases like cancer, birth defects and genetic damage are thus very dangerous water pollutants.

Non potable forms of waste water generated by humans may be referred to as grey water, which is treatable and thus easily able to make potable again and black water, which generally contains sewage. Grey water is defined as wastewater produced in bathtubs, showers, wash basins, laundry machines and kitchen sinks [3]. The primary contaminants present in grey water are surfactants, nitrates, chlorides, phosphates and sulphates. Grey water can hence be viewed as a valuable resource of nutrients and it can be used for horticultural and agricultural applications. The World Health Organization (WHO) estimates that safe water could prevent 1- 4 million child deaths from diarrhea in every year [4].

Some of trace elements play essential role in biological process, but at higher concentrations they may be toxic to the biota, they disturb the biochemical process and causes hazards. These elements include metals (Cd, Cr, Co, Cu, Zn, Pd, Hg, Ni and Ag) and metalloids (Se, As, Sb) most of the traced elements are transition metals with variable oxidation states and co-ordination number. These metals forms complexes with organisms in the environment there by increasing their mobility in the biota and main fest toxic effects [5-7].

Water pollution by organic compounds has increased tremendously due to increases in industrial and animal production activity. Color stuff discharged from industries poses certain hazards and environmental problems. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade. Furthermore, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities.

Textile industry use large number of dyes and pigments to color their products. There are more than 100,000 commercially available dyes with over 7x10^5 tones of dyestuff are produced annually. Many types of dye are used in textile industries such as direct reactive, acidic and basic dyes. Most of these dyes represent acute problems to the ecological system as they considered toxic and have carcinogenic properties which make the water inhibitory to aquatic life. The main sources of waste water generated by the textile industry originate from the washing and bleaching of natural fibers and from the dyeing and finishing steps. Given the great variety of fibers, dyes and process aids, these processes generate waste water of great chemical complexity and diversity, which are not adequately treated in conventional waste water treatment plant.

Waste water effluents from different industries such as textile rubber, paper and plastics, fertilizer, paints and pigments, wood pulp, printed circuit board, paints and pigments contains several kinds of synthetic dyestuffs [8], clay [9, 10], peat [11,], activated carbon [12-14], polymers [15,16], alumina [17,18], pesticides [19], radionuclide [20], dyes [21,22], cosmetics [23,24], pharmaceutical paint electroplating [25,26], printing carpet [27], battery manufacturing [28], chemical fertilizers, municipal sewage [29], painting, coating, mining, extractive metallurgy, nuclear [30], and other industries. Their removal has attracted much practical and academic interest, owing to increased concern with their environmental impact. The problems of the ecosystem are increasing with developing technology. Heavy metal pollution is one of the main problems. Toxic heavy metal compounds coming to the earth surface not only reach the surface water (seas, lakes, ponds and reservoirs), but also contaminate underground water in trace amount by leaking from the soil after rain and snow [31]. For the present study, the following dyes and metal ions were selected their properties are given in the following pages.

1.1.1. *Congo Red (CR): -*Congo red was first synthesized in 1883 by Paul Bottiger, who was working then for the Friendrich Bayer Company in Elberfield, Germany Congo red can be used as a pH indicator. Congo red is the sodium salt of 3, 3' [1, 1'-biphenyl] - 4, 4'-diyl) bis (4 – amino naphthalene -1-sulphonic acid). It is a secondary diazo dye. Congo red is water soluble; yielding a red colloidal solution, its solubility is better in organic solvents likes ethanol. Congo red containing effluents are generated from textiles, printing and dyeing, paper, rubber, plastic industries etc. due to its structural stability, it is difficult to biodegrade. The molecular formula is $C_{32}H_{22}N_6Na_2O_6S_2$ andmolecular weight is 696.66 gm. /mole [32, 33]. The chemical structure is shown in fig.1.

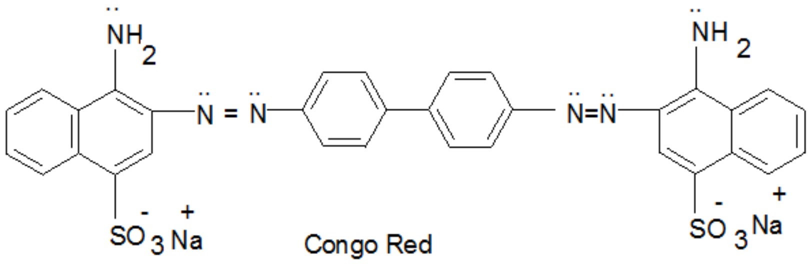

Figure: 1. Chemical structure of Congo red.

1.1.2. ***Methylene Blue (MB):*** -It is a heterocyclic aromatic chemical compound withthe molecular formula $C_{16}H_{18}N_3SCl$ molecular weight is 319.85 gm./mol. IUPAC name is 3,7-bis (Dimethylamino) phenothiazin-5-ium chloride. It was first prepared by German Chemist Heinrich Caro in 1876 [34]. It is a basic cationic dye, which is most commonly used for coloring. It is widely used as a redox indicator in analytical chemistry. It can also be used for printing calico, dyeing, printing cotton and tannin, indicating oxidation-reduction, dyeing leather and in purified zinc-free form. It is used as an antiseptic and for other medicinal purposes. It is also used in aqua-culture and by tropical fish hobbyists as a treatment for fungal infections. The Chemical structure of methylene blue is shown in figure 2.

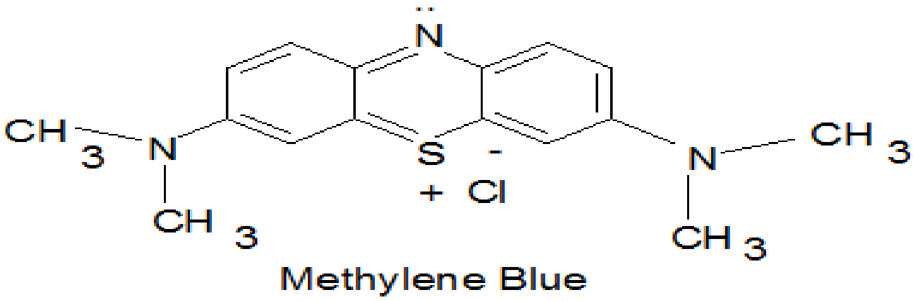

Figure: 2. Chemical structure of methylene blue

1.1.3. ***Chromium [Cr (VI)]:*** -The name of the element is derived from the Greek word "Chroma", meaning color, because many of its compounds are intensely colored. It is the 24th most abundant element in Earth's crust with an average concentration of 100 ppm Cr (VI) compounds are powerful oxidants at low or neutral pH. Chromates are often used to manufacture, amongst other things, leather products, paints, cement, mortar, anti-corrosives, tanning and electroplating and chrome-producing manufactures. It has led to increase in chromium content of waste water.

1.1.4. *Copper [Cu (II)]:* -Copper is present in the Earth's crust at a concentration of about 50 ppm most copper is mined or extracted as copper sulfides from large open pit mines in porphyry copper deposits that contain 0.4 to 1.0 % copper. It is essential to all living organisms as a trace dietary mineral because it is a key of constituent of the respiratory enzyme complex cytochrome-‘C’ oxidase and blood pigment hemocyanin. The major industries discharging copper in their effluents are electroplating, paper and pulp, petroleum refining and wood preservation. It is also used as a conductor of heat and electricity, as a building material, and a constitution of various metal alloys.

1.2. Techniques of Removal of Hazardous Materials:

Various physicochemical and biological methods have been studied for the toxic metal ions and organic chemicals from industrial wastewater such as ion-exchange, electro-deposition [35], solvent extraction [36], reverse osmosis, electro-dialysis [37], precipitation [38], sorption [39], Biological process [40], membrane based separation process [41], Chemical oxidation [42], Liquid-liquid extraction [43], coagulation [44], chelating ion exchangers [45], ultra-filtration, phyto-extraction [46], and adsorption etc. Most of these techniques require higher capital investment; drawback of chemical treatment is production of secondary pollutants due to excessive utilization of chemicals. Adsorption is the favored technique over others because of its easy availability, widely studied mechanism, ease of operation, simplicity in design, wider application and non-formation of by product [47, 48] as well as offering the potential for regeneration, recovery and recycling of the adsorbent material. Activated carbon is the most popular adsorbent for removal of dyestuffs from wastewater [49], However adsorbent grade carbon is cost prohibitive and both regeneration and disposal of the used carbon are often very difficult. Hence, the use of low-cost materials as possible removal of toxic heavy metal ions and organic compounds from aqueous solution has been highlighted recently. These materials come from agricultural products [50].

Literature survey reveals that agricultural bi-products are used for the adsorption studies such as. Bale tree leaf powder [51], Leaves of Cauliflower [52], Bajara powder [53], Soya been Husk [54], Jute [55], Sennauniflora [56], Coirpith [57], Oak wood sawdust [58], Hazelnut shell [59], Rice straw [60], Tamarind hull [61], Marine algal biomass [62], Pine Fruit [63], Almond husk [64], Banana Peel [65], Teak tree bark [66], Palm Kernel Coat [67], Papaya seeds [68], Babul Bark [69], Coconut leaves [70], Manaiferaindica [71] Yellow passion fruit peel [72] Neem leaves [73], Sawdust [74], Peat [75], Maize leaf [76], Banana pith [77].

1.3. Terms involved:

Adsorption is a process that occurs, when a gas or liquid solute accumulates on the surface of a solid or a liquid, forming molecular or atomic film. This process differs from absorption.

Adsorbate: **-**The material being concentrated or adsorbed on the surface is called the adsorbate.

Adsorbent: **-**The material which adsorbs the other material on its surface is called adsorbent.

Sorption: **-**The process in which both adsorption and absorption take place simultaneously is generally termed as sorption.

1.4. Types of Adsorption:

At molecular level, adsorption is due to attractions, interactions between a surface and the species being adsorbed. There are two main types of adsorption of molecules on surface and they are physical adsorption (physico-sorption) and chemical adsorption (Chemisorption).

1.4.1. Physical adsorption: -

Physical adsorption is a result of intermolecular forces of attraction between of attraction between molecules of the adsorbent and the adsorbate. In this case the adsorbate accumulates to the surface only through weak intermolecular (Van der Waals) interactions. It occurs at particular set of conditions and it is a reversible process. High physical adsorption can be obtained at temperature close to the critical temperature of the gas [78]. Physical adsorption often is a multilayer adsorption.

Extent of physical adsorption depends mainly on the surface area of adsorbent. The energy of interaction between adsorbent and the adsorbate has the same order of magnitudes as, but it is usually greater than the energy of condensation of the adsorptive. Therefore, no activation energy is needed. The adsorption enthalpy varies between 5-40 *KJ/mole*.

1.4.2. *Chemical adsorption: -*

Chemical adsorption is a result of chemical interaction between the solid and the adsorbed substance. It is also called activated adsorption. In chemical adsorption molecule accumulates to a surface through the formation of chemical bond. It is favored by higher temperature, because chemical reactions proceed more rapidly at elevated temperatures. It exhibits high energy of adsorption. It may be exothermic or endothermic process ranging from very small to very large magnitudes. Chemical adsorption is irreversible and occurs at high temperature. It forms monomolecular layer or unilayer in character. The adsorption enthalpy varies between 40-80 *KJ/mole* [79].

1.5. Factors Influencing the Adsorption:

The following factors are affected on adsorptions.

1.5.1. ***Temperature: -***Adsorption reactions are normally exothermic thus the extent of adsorption generally increases with decreasing temperature, i.e. adsorption is inversely proportional to temperature. Hence, according to Le-Chatelier's principle as the temperature increases, the adsorption has a tendency to go in the reverse direction. This means that the molecules adsorbed on the surface, will try to leave the surface.

1.5.2. ***Nature of adsorbent: -***The larger will be the area of adsorbent, the more willbe its adsorption. The physico-chemical nature of the adsorbent has profound effects on both rate and capacity for adsorption. It also depends on the nature of adsorbent. It is faster on rough surface, porous solids, more finely divided powder, colloidal particles etc.

1.5.3. ***Nature of adsorbate: -***The adsorption of solid surface takes place by the attraction of the adsorbate molecule due to its residual forces. The adsorption capacity of different substance depends on their effective areas.

1.5.4. ***Concentration of the adsorbate: -***The extent of adsorption of the solute fromthe solution is directly proportional to the concentration of the solution i.e. more concentrated the solution; more extensive the solute adsorption.

1.5.5. ***pH: -***It is an important parameter affecting adsorption from aqueous solution because of hydrogen and hydroxide ions are adsorbed quite strongly, the adsorptions of other ions are influence by the pH of the solution.In general adsorption of typical organic pollutant from water is increased with decreasing pH. The pH affects both the surface charge of a adsorbent, the degree of ionization of the heavy metal in solution and specification of the adsorbate. At higher H^+ concentration, the adsorbent surfaces become more positively charged thus reducing the attraction between adsorbent and metal ions. At higher pH the adsorbent surface takes more negatively charges, thus attracting more metal ions.

1.6. Theories of adsorption:

1.6.1. ***Langmuir adsorption theory-*** Irving Langmuir was the first to derive a scientifically based adsorption isotherm in 1918 [80]. The model applies to gases adsorbed on solid surfaces. It is the most common isotherm equation to use due to its simplicity and its ability to fit a variety of adsorption data.

Langmuir adsorption isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. There by the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases [81]. The Langmuir isotherm is valid for monolayer adsorption onto the surface containing a finite number of identical sites.

The linear form of the equation is given by,

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_0}\right) C_e + \frac{1}{bQ_0} \quad \text{or} \quad \frac{1}{q_e} = \left(\frac{1}{Q_0}\right) + \frac{1}{bQ_0C_e} \qquad (1)$$

Where, C_e (*mg/L*) is the equilibrium concentration of the adsorbate, q_e (*mg/g*) is the amount of adsorbate adsorbed per unit mass of adsorbent, at equilibrium, Q_0 (*mg/g*) and b (*L/mg*) are Langmuir constants related to maximum monolayer adsorption capacity and energy of adsorption respectively. The values of Q_0 and b are calculated from the slope and intercept of plot of $\frac{C_e}{q_e}$ against C_e respectively [82, 83]. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameterR_L. Which is a dimensionless constant referred to as separation factor or equilibrium parameter [84].

$$R_L = \frac{1}{1+bC_0} \tag{2}$$

Where, C_0 is initial concentration in ppm and b is Langmuir constant related to the energy of adsorption. R_LValue indicates the adsorption nature to be either unfavorable if R_L> 1, linear if R_L= 1, favorable if 0 <R_L< 1 and irreversible if, R_L= 0 [85].

1.6.2. ***Freundlich adsorption isotherm theory:*** -The first mathematical fit to anisotherm was published by Freundlich and Kuster in 1894, and is a purely empirical formula for gaseous adsorbates.

$$\frac{x}{m} = K_f P^{1/n} \tag{3}$$

Where, *x* is the quantity adsorbed, *m* is the mass of the adsorbent, *P* is the pressure of adsorbate and K_f and *n* are empirical constants for each adsorbent- adsorbate pair at a given temperature.

Freundlich presented an empirical adsorption isotherm for non-ideal sorption on heterogeneous surfaces as well as multilayer sorption and is also expressed as

$$\frac{x}{m} = K_f {C_e}^{1/n} \tag{4}$$

Where C_e is the equilibrium concentration of adsorbate (*mg/L*), The constants K_f and *n* can be obtained by taking *log* on both sides of equation (4) as follows,

$$\log\frac{x}{m} = \frac{1}{n}\log C_e + \log K_f \tag{5}$$

The constant K_f is an approximate indicator of adsorption capacity, while $\frac{1}{n}$ is a function of the strength of adsorption in the adsorption process [86]. If $n = 1$ then the partition between the two phases is independent of the concentration. If value of $\frac{1}{n}$ is below one, it indicates a normal adsorption, on the other hand $\frac{1}{n}$ being above one indicates co-operative adsorption [87]. A plot of $\log\frac{x}{m}$ against $\log C_e$ gives a straight line with an intercept on the ordinate axis. The value of *n* and K_f can be obtained from the slope and the intercept of the linear plot. The value of *n* is greater than unity, (1<*n* <10), that means favorable adsorption [88].

1.7. Thermodynamic Parameters:

. Thermodynamic Parameters such as Gibb's free energy change ΔG^0, enthalpy change $\Delta H^0$and entropy change ΔS^0 were determined using the following equations [89-92].

$$K_c = \frac{C_{ad}}{C_e} \tag{6}$$

$$\Delta G^0 = -\,RT \ln K_c \tag{7}$$

Where, $\Delta G^0 = \Delta H^0 - T\Delta S^0$ (8)

$$\log K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \tag{9}$$

Where, K_c is the equilibrium constant, C_{ad} is the amount of dye adsorbed per liter of the solution at the equilibrium, C_e is the equilibrium concentration (*mg/L*) of the metal in the solution, *T* is the temperature in Kelvin and *R* is the gas constant (*8.314 J/mole*). The values of ΔH^0 and ΔS^0 were determined from the slopes and intercepts of the plot of $\log K_c$ against $\frac{1}{T}$ respectively.

The Gibb's free energy change indicates the degree of spontaneity of the adsorption process. The negative value of ΔG^0 indicates that the adsorption is favorable and spontaneous [93, 94]. The positive value of ΔH^0 indicates physisorption and endothermic nature of adsorption, while negative value of ΔH^0 suggests that the adsorption is exothermic [95, 96]. The positive value of ΔS^0suggests that the increased disorder and randomness at the solid solution interface with adsorption.

1.8. Kinetic model of adsorption:

Kinetic studies are significant for any kind of adsorption process. A kinetics study was carried out to determine the equilibrium time required for the uptake of metals from a liquid solution. Adsorption kinetics not only describes the adsorption mechanism but also describes the adsorption rate which controls the contact time of adsorbate at the solid-liquid interface [97]. The adsorption mechanism depends on the physical and chemical characteristics of adsorbent and adsorbate, pH of medium, temperature, contact time and mass transport process [98]. Various kinetic models can be suggested for an adsorption including the Lagergren pseudo-first order kinetics, pseudo-second order kinetics, liquid diffusion model and intra-particle diffusion model [99-100]. Pseudo-first order kinetics is present to describe the rate of adsorption process in liquid-solid phase. The Lagergren pseudo-first order rate equation is given as,

$$\frac{dq}{dt} = K_1(q_e - q_t) \tag{10}$$

After definite integration by applications of the conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$ Equation (10) becomes,

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{11}$$

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \tag{12}$$

Where, q_e (*mg/gm*) is the amount of adsorption at equilibrium, q_t (*mg/gm*) denotes the amount of adsorption at time *t* (*min.*) and K_1 (*min^{-1}*) is the rate constant of the pseudo-first order model. Based on experimental results, linear graphs were plotted between $\log(q_e - q_t)$ versus t, to calculate K_1, q_e and R^2.

The Kinetics data were also analyzed by pseudo-second order equation. The pseudo-second order equation is developed by Ho can be written as

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \tag{13}$$

Where, K_2 (*gm.mg^{-1}min^{-1}*) is the rate constant of the pseudo-second order. Integrating equation (13) for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$ gives

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_2 t \tag{14}$$

The linear form of equation is

$$\frac{t}{q_t} = \frac{1}{K_2\, q_e^2} + \frac{1}{q_e} \mathrm{t} \tag{15}$$

K_2 and q_e can be obtained from the intercept and slope of plotting t/q_t against t . Pseudo-second order adsorption rate constant is used to estimate the activation energy by using Arrhenius equation

$$\ln K = \ln A - \frac{E_a}{RT} \tag{16}$$

$$\log K = \log A - \frac{E_a}{2.303RT} \tag{17}$$

Where A is pre-exponential factor ($gm.mg^{-1}min^{-1}$) E_a is the activation energy of adsorption (*KJ/mole*) E_a value can be determined by plotting graph $\log K$versus $\frac{1}{t}$ a straight line with slope $-\frac{E_a}{2.303R}$ and intercept is $\log A$.

1.9. Selected adsorbent:

For the present work low-cost agricultural adsorbent was selected from Rauwolfia serpentine (Sarpgandha) shrub is used to adsorption of heavy metal ions as well as organic dyes. It is large climbing shrub, found in the tropical regions in south India. The roots are used as medicine. It is being extensively used in reducing blood pressure in hyperplesis and as a sedative in the treatment of insomnia, hypochondria, mental disorders and certain forms of insanity. Its leaves when freshly ground and applied to the toes, could serve as an antitodes for snake poison.

Fig : 3. Sarpgandha **(***Rauwolfia serpentine***)** shrub**.**

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2. Experimental Details

2.1. Analytical methods:

For the present study all reagents used were of analytical grade, double distilled water was used for preparation of solutions. The following standard materials have been used as reagents, methylene blue (CI: 52015, MW: 319.85 gm.), was supplied by Qualigens, Fine Chemicals, Mumbai (India) and Congo red (CI: 22120, MW: 696.66 gm.) were Supplied by Loba Chemicals Pvt. Ltd. Mumbai (India); potassium dichromate ($K_2Cr_2O_7$) and copper sulphate pentahydrate ($CuSO_4.5H_2O$) diphenyl carbazide ($(C_6H_5NH.NH_2)CO$), sodium diethyl dithiocarbamate, supplied by Oxford Laboratory Mumbai, citric acid, ethylene diamine tetra acetic acid (EDTA), butyl acetate , ammonia were supplied by Qualigens Thermo Fisher Scientific India Pvt. Ltd., Mumbai. Concentrations of adsorbates like Congo red (CR), methylene blue (MB), chromium (VI) and copper (II) metal ions were measured at the wavelength of their maximum absorbance (λ max) that was determined by UV-Visible single beam Spectrophotometer, (BioEra: Cal No.BI/CI/SP/SB-S-03). The pH was measured by digital pH-meter (Elico: LI 615).

2. 2. Calibration of glassware and Instruments:

2.2.1. Calibration of glassware: - To minimize error associated with measurement. These are used to find out error in measurement of the volume of the glassware. We can calibrate the volumetric glassware that is measure the real volume of solution delivered or contained by weighing mass of the water. Weighing can be done with very good accuracy and knowing water density, we can calculate volume of given water mass.

2.2.1.1. Volumetric flask calibration: -

Before use, volumetric flask was cleaned thoroughly and dried by using hot air blower and stoppered. Weight of the clean and empty dried volumetric flask was taken on an analytical balance. The volumetric flask was filled with distilled water at room temperature to just below the mark; carefully water was added with a disposable pipette until the bottom of the meniscus coincides with the calibration line. A droplet of water present above the line was removed with a lintless towel or a strip of filter paper. The flask was weighed. Immediately after weighing the temperature of the water in the flask was measured and record. The true volume of flask obtains at least three measurements by emptying the flask and drying it between measurements was calculated.

2.2.1.2. Calibration of pipette: -

Pipette can be calibrated by weighing the water delivered from them. The clean and dry Erlenmeyer flask was taken for the calibration of pipette. In order to obtain meaning full results proper techniques for delivering the water must be follows.

Using a bulb, distilled water was drowning up until the calibrated volume is full and the water level is slightly above the calibration mark. With a finger over the upper end of the pipette, the pipette was lifted out of the water, tilted the pipette almost to the horizontal and wiped any residual water from the outside walls. The pipette upright turned and the water was allowed to drain slowly until the meniscus is exactly at the calibration line. The hanging drop was removed by touching it to the side of a glass vessel. The pipette was hold vertically and the water was allowed to drain with the pipette tip against the wall of the flask into the pre-weighed Erlenmeyer’s flask and, making sure to remove the suspended drop, the flask was stoppered and weighed it to the analytical balance. The process was repeated several times until consistent results are obtained for at least 5-6 measurements. From the mass of the water for each calibration measurement, the true volume delivered by your pipette was calculated.

2.2.1.3. Calibration of a Burette: -

The burette was filled with water. The water was drained into a beaker until it is at, or just below, the zero mark. After 10-20 seconds for drainage. The burette was allowed to stand for 5 minutes and then the volume was recorded. No noticeable change in the reading was observed. Once the tightness of the stopcock is assured, the burette was refilled and again drain into a waste until it is at, or just below, the zero mark. The tip of the burette was in contact with the wall of the waste beaker to remove the pendent drop of water. The volume was recorded. A receiving container was weighed on the analytical balance. About 5 mL of water was drained from the burette into the beaker, allowed for 10-20 seconds for drainage. The tip of the burette was touched to the wall of the beaker to again remove the pendent drop. Read the burette and weighed the water. The actual volume of water delivered by the burette was calculated. The procedure was repeat at least once more.

2.2.1.4. Graduated Cylinder Calibration: -

A clean, dry graduated cylinder on the lab scales was placed and its mass was record. It was removed from lab scales. Some tap water poured into the graduated cylinder. Any water bubbles removed from the liquid first and then removed any droplets from the inside or outside of the cylinder. Using the graduations on the cylinder, the volume was read precisely as possible and recorded. The cylinder was placed on the scales and the mass of the water calculated.

2.2.2. Calibration of Instruments:

2.2.2.1.Calibration of Spectrophotometer: -

UV-Visible Spectrophotometers are widely used by many laboratories including those found in academia and research as well as industrial quantity assurance. The technique is mainly used quantitatively the wavelength of light which emitted onto the sample was first determined. This was done by setting the wavelength at value from 400 to 800 nm. Two cells were rinsed and the absorbance was adjusted to zero. The reference cell was left in the part. The sample cell was emptied and filled with a known concentration of solution. The spectrum was scanned between 400 to 800 nm, and the wave length at which maximum absorbance was determined. The Spectrophotometer was then set to this wavelength and the absorbance of the solutions was measured. The concentration of the sample solution was obtained by the use Lambert's-Beer's law,

$$\log \frac{I_0}{I} = \varepsilon c t$$

$$A = \varepsilon c t \qquad \left(A = \log \frac{I_0}{I} \right)$$

Where, I_0 is the intensity of incident light, I is the intensity of transmitted light, c is the concentration of solution, t is the thickness of the medium (1cm.), ε is the molar absorption coefficient for concentration (moles/lit) and A is the absorbance.

A calibration curve was created for each reagent by using known concentration, the absorbance from a series of samples of those concentrations was measured and a plot was made of absorbance against concentration. The calibration curve then was used to identify the concentration of an unknown samples (before absorption) of known concentration was measured in order to determine the actual concentration of the sample remaining in the solution. Then from the difference in the concentrations the amount of the sample adsorbed at any stage of the adsorption was calculated [1].

2.2.2.2. Calibration of pH-meter: -

The pH meter was calibrated properly by using following procedure.

pH electrode was rinsed by using tap water. The outside of the electrode was dried but blot the bottom of the sensitive glass with a paper towel. This was done to avoid abrasion of the glass measuring end and to prevent dilution of subsequent use. pH electrode was placed into a buffer solution having pH 7.0. For most electrodes this means an immersion of only 1 to 2 inches. Magnetic stir plate was used for more precise lab work. Turn the meter on and selected the calibration mode. The temperature of the solution was read and the temperature compensate control was set at measured temperature. The range selector switch to pH range 0 – 9 positions was set. If the electrode is in good condition, the value will jump to near the buffer value very rapidly. As the electrode deteriorates or if dirty/clogged, this process will take longer. That was the standardization of pH meter in neutral range. Similarly, the pH was measured using another buffer of pH 4.01 and pH 9.2. Once the calibration at two or more points has been completed, the meter will automatically return to the normal measuring mode. It will show the temperature compensated value of the solution. Some small variation may occur depending upon the inherent accuracy of the meter and the variation of temperature. If the probe and the solution are at different temperatures, readings will continue to change slightly as the two-reach equilibrium [2].

2.3. Preparation of adsorbents:

The low-cost agricultural adsorbents were prepared from leaves of *Rauwolfia serpentine* (Sarpgandha) shrub was used. This adsorbent was used without any chemical- treatment for adsorption of heavy metal ions as well as organic dyes.

The mature and fresh leaves of *Rauwolfia serpentine* (Sarpgandha) shrub were collected from College campus and washed thoroughly by distilled water before drying to remove any dust then dried in shadow region [3]. The dried leaves were grinded to fine powder [4]. The homogeneous powder was obtained by passing through mesh of desired particle size (40 – 70 µm). The homogeneous fine powder adsorbent was stored in an air tight container for the adsorption study for further experiments.

2.4. Preparation of adsorbates:

The adsorbates selected for the present study were, the organic compounds such as Congo red, and Methylene Blue and the inorganic compounds (metal ions) were Chromium [Cr (VI)] and Copper [Cu (II)].

2.4.1. Organic compounds: -

All the above organic compounds (Congo Red, and Methylene Blue) are commercially available and these are purchased from different chemical laboratories such as methylene blue were purchased from Qualigens, Fine Chemicals, Mumbai (India), Congo red was purchased from Loba Chemicals Pvt. Ltd. Mumbai (India). All solutions were prepared in double distilled water. The concentration of dye solutions was determined by using UV-Visible single beam Spectrophotometer, (BioEra: Cal No.BI/CI/SP/SB-S-03). Stock solutions (500 ppm) were prepared by dissolving weighed quantities of these organic compounds (500 mg) in double distilled water (1000 ml). The experimental solutions were prepared by successive dilution using double distilled water. The solutions were carried out from the stock solution to prepare solutions in different concentrations [5]. The concentration of solution was determined from calibration curve spectrophotometrically at their λmax that is Congo Red (λmax = 510 nm), and for Methylene Blue (λmax = 570 nm).

2.4.2. Inorganic compounds (Metal ions):-

2.4.2.1. Chromium [Cr (VI)]: - Stock solution of chromium metal ion (500 ppm) was prepared by weighing and dissolving 1.4140 gm. of potassium dichromate ($K_2Cr_2O_7$) in one liter of double distilled water in graduated volumetric flask. The dilutions were carried out from the stock solution to prepared desired concentrations, in order to standard the solution. 10 ml of chromium sample solution was transferred to 25 ml standard flask; enough H_2SO_4 was added to make acid concentration 0.2 N on dilution up to 25 ml. Now add one ml of diphenylcarbazide [$(C_6H_5NH.NH_2)$ CO] solution, it was shacked till it got mixed with the solution, allow the solution to stand for 10 – 15 minutes. And then absorbance was determined at 540 nm. Using a reagent blank as compared liquid [6].

2.4.2.2. Copper [Cu (II)]: -Stock solution of chromium metal ion (500 ppm) was prepared by weighing and dissolving 1.965 gm. of copper sulphate pentahydrate ($CuSO_4.5H_2O$) in one liter of double distilled water in graduated volumetric flask and used to prepare different solutions. 10 ml of copper sulphate pentahydrate sample solution was transferred to 100 ml beaker; and 5 ml of 25 % aqueous citric acid solution was added to it. The solution was made slightly alkaline by the addition of dilute ammonia solution and then boiled to remove excess of ammonia.15 ml of 4% EDTA solution was added then it was cooled to room temperature and transferred to a separating funnel. 10 ml of 0.2 % aqueous sodium diethyl dithiocarbamate solution was added with constant shaking for 45 seconds. A yellow brown colour was developed into the solution.

20 ml of butyl acetate (ethanoate) was added into the funnel and the solution shakes for 30 seconds. The organic layer acquires yellow coloration. The content agitated for 15 seconds the phase obtained were allowed to separate. The lower aqueous layer was removed. 20 ml of 5 % sulphuric acid (v/v) was added with constant shaking for 15 seconds, it was cooled thus separate organic phase. The absorbance was determined at 560 nm against blank was determined.

2.5. Parameters for Batch Adsorption Techniques:

2.5.1. Effect of contact Time: - Contact time is one of the important parameters

For the assessment of practical application of adsorption process [7-10]. Adsorbent powder was mixed with different adsorbate solution in a glass bottles, then stirred for required time period with the help of mechanical stirrer at room temperature, the samples were filtered and its absorbance was then measured. The concentration was to be measured after 10, 20, 30, 40, 50, 60 minute and 24 hrs. time interval. The contact time process was repeated at different time's intervals. The other parameters such as adsorbent dose, concentration of adsorbate, temperature, pH and amount of salt were kept constant. The amount of adsorbed (mg/g) was calculated using the formulae reported by Vanderborght and Van Griekenm [11], and then the kinetic adsorption parameters were calculated.

$$q=\frac{V(Co-Ct)}{M} \tag{1}$$

Where, q is the amount of solute adsorbed from the solution *(mg/ g)*, *Co*is the concentration before adsorption *(mg/L)*, and*Ct* is concentration after adsorption. *V* is the volume of adsorbate*(L)* and *M* is the weight of the adsorbent *(gm).*

2.5.2. Effect of amount of adsorbent: - Adsorption isotherms have many Important practical applications, for instance, it provides information on how adsorption system proceeds, and indicates how efficiently given adsorbent interacts with adsorbate. It also helps to estimate economic feasibility of an adsorbent for specific commercial applications. There are a number of factors that determine the shape of isotherm. The isotherm equations like Langmuir and Freundlich have been tested in order to describe the equilibrium characteristics of adsorption. Adsorbent dose is one of the important factors because it is used to determine capacity of an adsorbent for initial concentration of adsorbate [12].

2.5.3. Effect of initial concentration of adsorbate: - Effect of initial concentration of organic and metal ion solution is a major part of the study. By varying the concentration of organic and metal ion solution and keeping the amount of adsorbent constant at constant temperature, the time growth studies of adsorption were undertaken [13]. The percentage adsorption was calculated by following equation;

$$\text{Percentage adsorption} = \frac{(C_0 - C_e)}{C_0} * 100 \tag{2}$$

Where, C_0 and C_e are the initial and equilibrium concentrations respectively.

2.5.4. Effect of Temperature: -Temperature is one of the most important factors which determine the extent of adsorption of given system. The adsorption experiments were performed at four different temperatures *viz.*,10 ,20, 30, and 40 °C above room temperature in thermostat. The study was maintained at constant temperature and was shaken continuously till the equilibrium was attained. The sample solutions were filtered at different time intervals was used for measuring the corresponding concentration remaining in the solution. The obtained values were employed for calculating the actual amount of organic dyes and toxic heavy metal ions adsorbed on the surface of adsorbents at that time. The experiments were carried out at different temperature to study the effect of temperature on adsorption and to determine thermodynamic parameters such as Gibb's free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) [14-16].

2.5.5. Effect of pH: -The initial pH of the solution is an important parameter,

Which controls the adsorption process, particularly the adsorption capacity [17]. For this set of experiments the initial pH of solution was taken as 1.0 to 11.0. The pH was adjusted with the help of HCl (0.1 N) and NaOH (0.1 N) [18] solution. Then the adsorbent powder was (0.5 gm.) was mixed with 50 ml of adsorbate solution at 30-minute time, after 30 minutes the samples were filtered and analyzed.

pH of the solution changes due to the surface charge of the adsorbent, the degree of ionization of the adsorptive molecule and extent of dissociation of functional groups on the active sites of the adsorbent [19].

2.5.6. Zero Point pH: -The determination of the pHpzc of the samples was carried out taking 20 cm^3 of adsorbate solution and adds KCl (0.1 M) in closed Erlenmeyer flask. The pH was adjusted to a value between 2 - 11 by adding HCl 0.1 M or NaOH 0.1 M solutions. Then, 0.02 gm. sample was added and the final pH measured after 24 hrs. under agitation at room temperature. The pH_{pzc} is the point where the curve pH_{final}againstp$H_{initial}$ crosses the line $pH_{initial} = pH_{final}$. Similarly, the $pH_{pzc}$was also determined for all samples using the above method [20].

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3. Experimental Results

3.1. Adsorption Study of Congo red (CR) Dye on Sarpgandha (*Rauwolfia serpentine*) Leaves Powder (SLP) Low-Cost Adsorbent: -

3.1.1. Effect of Contact time: -

Table: 3.1.1. Absorbance and Concentrations of CR dye solution at different time interval.

Amount of adsorbent = 1.0 g. Conc. of adsorbate = 20 ppm

Volume of adsorbate = 100 mL pH = 6.4 Temperature = 300.5±.3 k

Time (min.)	Absorbance and concentrations of Sarpgandha (Rauwolfia serpentine) adsorbent at different time interval.	
	Congo red dye	
	Absorbance	Concentration
10	1.203	8.4718
20	1.017	7.162
30	0.941	6.6268
40	0.924	6.507
50	0.917	6.4577
60	0.913	6.4296
24 Hrs.	0.618	4.3521

3.1.2. Effect of Adsorbent Dose: -

Table: 3.1.2. Absorbance and Concentration of CR dye solution at different adsorbent dose of SLP with time interval.

Concentration of adsorbate = 20 ppm. Temperature = 300.5±0.3 k

Volume of adsorbate = 100 mL pH = 6.4

Time (min.)	Absorbance and Concentration of CR dye solution at different adsorbent dose.									
	0.5 g		**1.0 g**		**1.5 g**		**2.0 g**		**2.5 g**	
	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.
10	1.354	9.54	1.213	8.54	1.173	8.26	1.149	8.09	1.131	7.96
20	1.198	8.44	1.023	7.20	0.967	6.81	0.938	6.61	0.927	6.53
30	1.184	8.34	0.947	6.67	0.912	6.42	0.872	6.14	0.859	6.05
40	1.163	8.19	0.929	6.54	0.884	6.23	0.843	5.94	0.837	5.89
50	1.151	8.11	0.922	6.49	0.868	6.11	0.831	5.85	0.829	5.84
60	1.145	8.06	0.919	6.47	0.863	6.08	0.827	5.82	0.824	5.80
24 Hrs	1.134	7.99	0.589	4.15	0.365	2.57	0.264	1.86	0.208	1.46

3.1.3. Effect of Initial Concentration: -

Table: 3.1.3. Absorbance and Concentration of CR dye solution at different initial concentration of CR dye solution with time interval

Amount of adsorbent = 1.0 g Temperature = 300.5±0.3 k

Volume of adsorbate = 100 mL pH = 6.4

Time (min)	Absorbance and Concentration of Congo red dye solution at different initial conc.							
	5 ppm		**10 ppm**		**15 ppm**		**20 ppm**	
	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.
10	0.286	2.01	0.583	4.11	0.919	6.47	1.228	8.65
20	0.249	1.75	0.514	3.62	0.857	6.04	1.152	8.11
30	0.227	1.60	0.479	3.37	0.837	5.89	1.128	7.94
40	0.222	1.56	0.465	3.27	0.825	5.81	1.119	7.88
50	0.219	1.54	0.459	3.23	0.817	5.75	1.112	7.83
60	0.217	1.53	0.456	3.21	0.813	5.73	1.109	7.81
24 Hrs	0.179	1.26	0.405	2.85	0.711	5.01	0.991	6.98

3.1.4. Effect of Temperature: -

Table: 3.1.4. Absorbance and Concentration of CR dye solution at different temperature with time interval.

Amount of adsorbent = 1.0 g Conc. of adsorbate = 20 ppm.

Volume of adsorbate = 100 mL pH = 6.4

Time (min.)	Absorbance and Concentration of CR dye solution at different temperature.									
	305.5 k		**310.5 k**		**315.5 k**		**320.5 k**		**325.5 k**	
	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.
10	1.312	9.24	1.351	9.51	1.365	9.61	1.384	9.75	1.436	10.1
20	1.178	8.30	1.219	8.58	1.234	8.69	1.251	8.81	1.272	8.96
30	1.156	8.14	1.173	8.26	1.189	8.37	1.198	8.44	1.259	8.87
40	1.148	8.08	1.158	8.15	1.173	8.26	1.195	8.42	1.254	8.83
50	1.141	8.04	1.149	8.09	1.167	8.22	1.189	8.37	1.245	8.77
60	1.138	8.01	1.144	8.06	1.163	8.19	1.184	8.34	1.241	8.74
24 Hrs.	1.021	7.19	1.047	7.37	1.052	7.41	1.086	7.65	1.143	8.05

3.1.5. Effect of pH:-

Table: 3.1.5. Absorbance and Concentration of CR dye solution at different pH with time interval.

Amount of adsorbent = 1.0 g Conc. of adsorbate = 20 ppm.

Volume of adsorbate = 50 mL Temperature = 300.5± 0.3 k

No.	pH	Absorbance and Concentration of CR dye solution at different pH.			
		30 min.		**24 Hrs.**	
		Absorbance	Concentration	Absorbance	Concentration
1	2	0.483	3.40	0.295	2.08
2	3	0.827	5.82	0.534	3.76
3	4	0.876	6.17	0.712	5.01
4	5	0.942	6.63	0.768	5.41
5	6	0.924	6.51	0.859	6.05
6	7	0.931	6.56	0.883	6.22
7	8	0.941	6.63	0.928	6.53
8	9	0.948	6.68	0.934	6.58
9	10	0.955	6.73	0.939	6.61
10	11	0.959	6.75	0.942	6.63

3.1.6. Effect of Zero Point pH: -

Table: 3.1.6. Effect of Zero Point pH at different initial pH of CR

Amount of adsorbent = 0.02 g Conc. of adsorbate = 20 ppm.

Volume of adsorbate = 50 mL Temperature = 300.5± 0.3 k

Initial pH	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00	11.00
pH after 24 Hrs.	2.09	3.28	4.76	5.60	6.29	6.65	7.01	7.24	8.25	9.39
ΔpH	-0.09	-0.28	-0.76	-0.60	-0.29	0.35	0.98	1.76	1.75	1.61

3.2. Adsorption Study of Methylene blue (MB) on Sarpgandha (*Rauwolfia serpentine*) Leaves Powder (SLP) Low-Cost Adsorbent: -

3.2.1. Effect of Contact time: -

Table: 3.2.1. Absorbance and Concentration of MB dye solution at different time interval.

Amount of adsorbent = 1.0 g. Conc. of adsorbate = 100 ppm.

Volume of adsorbate = 100 mL. pH = 7.2 Temperature = 300.9 ± 0.3 k.

Time (min.)	Absorbance and concentrations of Sarpgandha (Rauwolfia serpentine) adsorbent at different time interval.	
	Methylene blue dye	
	Absorbance	Concentration
10	1.723	35.16
20	1.219	24.88
30	1.132	23.10
40	1.091	22.27
50	1.076	21.96
60	1.064	21.71
24 Hrs.	0.913	18.63

3.2.2. Effect of Adsorbent Dose:

Table:3.2.2. Absorbance and Concentration of MB dye solution at different adsorbent dose of **SLP** with time interval.

Concentration of adsorbate = 100 ppm Temperature = 300.9±0.3 k.

Volume of adsorbate = 100 mL pH = 7.2

Time (min.)	Absorbance and Conc. of MB dye solution at different adsorbent dose.									
	0.5 g.		**1.0 g.**		**1.5 g.**		**2.0 g.**		**2.5 g.**	
	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.
10	1.943	39.65	1.727	35.24	1.642	33.51	1.548	31.59	1.481	30.22
20	1.799	36.71	1.187	24.22	1.121	22.88	1.072	21.88	1.026	20.94
30	1.756	35.84	1.139	23.24	1.056	21.55	1.016	20.73	0.963	19.65
40	1.723	35.16	1.115	22.76	1.013	20.67	0.985	20.10	0.919	18.76
50	1.716	35.02	1.099	22.43	0.987	20.14	0.963	19.65	0.894	18.24
60	1.713	34.96	1.087	22.18	0.979	19.98	0.958	19.55	0.887	18.10
24 Hrs	1.596	32.57	0.586	11.96	0.353	7.204	0.251	5.122	0.197	4.02

3.2.3. Effect of Initial Concentration: -

Table: 3.2.3. Absorbance and Concentration of MB dye solution at different initial conc. of MB dye solution with time interval.

Amount of adsorbent = 1.0 g   Temperature = 300.9±0.3 k

Volume of adsorbate = 100 mL   pH = 7.2

Time (min.)	Absorbance and Concentration of MB dye solution at different initial conc.							
	25 ppm		**50 ppm**		**75 ppm**		**100 ppm**	
	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.
10	0.429	8.755	0.866	17.67	1.321	26.96	1.734	35.39
20	0.264	5.388	0.564	11.51	0.873	17.82	1.185	24.18
30	0.256	5.224	0.547	11.16	0.851	17.37	1.152	23.51
40	0.253	5.163	0.529	10.8	0.837	17.08	1.149	23.45
52	0.249	5.082	0.518	10.57	0.821	16.76	1.133	23.12
60	0.246	5.02	0.512	10.45	0.816	16.65	1.128	23.02
24 Hrs	0.195	3.98	0.405	8.265	0.664	13.55	0.933	19.04

3.2.4. Effect of Temperature: -

Table: 3.2.4. Absorbance and Concentration of MB dye solution at different temperature with time interval.

Amount of adsorbent = 1.0 g   Conc. of adsorbate = 100 ppm.

Volume of adsorbate = 100 mL   pH = 7.2

Time (min)	Absorbance and Concentration of MB dye solution at different temperature.									
	305. 9 k		**310. 9 k**		**315. 9 k**		**320. 9 k**		**325. 9 k**	
	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.
10	1.784	36.41	1.817	37.08	1.874	38.24	1.916	39.10	1.993	40.67
20	1.233	25.16	1.385	28.27	1.423	29.04	1.491	30.43	1.542	31.47
30	1.179	24.06	1.282	26.16	1.302	26.57	1.336	27.27	1.389	28.35
40	1.161	23.69	1.246	25.43	1.285	26.22	1.311	26.76	1.364	27.84
50	1.155	23.57	1.238	25.27	1.273	25.98	1.297	26.47	1.352	27.59
60	1.149	23.45	1.231	25.12	1.268	25.88	1.292	26.37	1.349	27.53
24 Hrs	0.916	18.69	0.973	19.86	1.007	20.55	1.064	21.71	1.091	22.27

3.2.5. Effect of pH: -

Table: 3.2.5. Absorbance and Concentration of MB dye solution at different pH with time interval.

Amount of adsorbent = 1.0 g Conc. of adsorbate = 100 ppm.

Volume of adsorbate = 50 mL Temperature = 300.9±0.3 k.

Sr. No	pH	Absorbance and Concentration of MB dye solution at different pH			
		30 min.		**24 Hrs.**	
		Absorbance	Concentration	Absorbance	Concentration
1	2	0.705	14.39	0.394	8.041
2	3	0.962	19.63	0.702	14.33
3	4	1.251	25.53	0.973	19.86
4	5	1.406	28.69	1.122	22.9
5	6	1.523	31.08	1.346	27.47
6	7	1.671	34.1	1.449	29.57
7	8	1.712	34.94	1.502	30.65
8	9	1.767	36.06	1.491	30.43
9	10	1.812	36.98	1.503	30.67
10	11	1.801	36.76	1.517	30.96

3.2.6. Effect of Zero Point pH: -

Table: 3.2.6. Effect of Zero Point pH at different initial pH

Amount of adsorbent = 0.02 g Conc. of adsorbate = 100 ppm.

Volume of adsorbate = 50 mL Temperature = 300.9±0.3 k

Initial pH	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00	11.00
pH after 24 Hrs.	2.771	3.783	4.672	5.581	6.285	6.274	6.892	7.871	8.724	9.716
ΔpH	-0.77	-0.78	-0.67	-0.58	-0.29	0.726	1.108	1.129	1.276	1.284

3.3. Adsorption Study of Chromium [Cr (VI)] Metal Ion on Sarpgandha (Rauwolfia Serpentine) Leaves Powder (SLP) Low-Cost Adsorbent: -

3.3.1. Effect of Contact time: -

Table: 3.3.1. Absorbance and Concentrations of Cr (VI) ions at different time interval

Amount of adsorbent = 1.0 g Conc. of adsorbate = 5 ppm.

Volume of adsorbate = 100 mL pH = 6.9 Temperature = 301.5 ± 0.3 k

Time (min.)	Absorbance and concentrations of Sarpgandha (Rauwolfia serpentine) adsorbent at different time interval.	
	[Cr (VI)] metal ion	
	Absorbance	Concentration
10	0.679	2.616
20	0.402	1.549
30	0.354	1.364
40	0.332	1.279
50	0.327	1.260
60	0.325	1.252
24 Hrs.	0.278	1.071

3.3.2. Effect of Adsorbent Dose: -

Table: 3.3.2. Absorbance and Concentrations of Chromium [Cr (VI)] metal ion at different adsorbent dose of **SLP** with time interval.

Conc. of adsorbate = 5 ppm Temperature = 301.5±0.3 k

Volume of adsorbate = 100 mL pH = 6.9

Time (min)	Absorbance and Conc. of Chromium metal ions at different adsorbent dose.							
	0.5 g		**1.0 g**		**1.5 g**		**2.0 g**	
	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.
10	1.057	4.072	0.706	2.720	0.678	2.612	0.638	2.458
20	0.929	3.579	0.526	2.026	0.491	1.891	0.375	1.445
30	0.922	3.552	0.491	1.891	0.453	1.745	0.352	1.356
40	0.913	3.517	0.474	1.826	0.416	1.602	0.337	1.298
50	0.902	3.475	0.461	1.776	0.402	1.549	0.331	1.275
60	0.897	3.455	0.457	1.760	0.397	1.529	0.328	1.263
24 Hrs	0.757	2.916	0.501	1.930	0.368	1.418	0.287	1.106

3.3.3. Effect of Initial Concentration: -

Table: 3.3.3. Absorbance and Conc. of Chromium [Cr (VI)] metal ion solution at different initial Conc. of solution with time interval.

Amount of adsorbent = 1.0 g Temperature = 301.5±0.3 k

Volume of adsorbate = 100 mL pH = 6.9

Time (min.)	Absorbance and Conc. of Cr (VI) metal ion solution at different initial conc.							
	5 ppm		**10 ppm**		**15 ppm**		**20 ppm**	
	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.
10	0.417	1.606	0.878	3.382	1.357	5.227	1.904	7.334
20	0.315	1.213	0.705	2.716	1.083	4.172	1.583	6.098
30	0.273	1.052	0.624	2.404	0.956	3.683	1.408	5.424
40	0.268	1.032	0.601	2.315	0.938	3.613	1.386	5.339
50	0.264	1.017	0.597	2.300	0.926	3.567	1.375	5.297
60	0.261	1.005	0.593	2.284	0.923	3.555	1.367	5.266
24 Hrs	0.224	0.863	0.482	1.857	0.776	2.989	1.124	4.330

3.3.4. Effect of Temperature: -

Table: 3.3.4. . Absorbance and Conc. of Chromium [Cr (VI)] metal ion Solution at different temperature with time interval

Amount of adsorbent = 1.0 g Conc. of adsorbate = 5 ppm.

Volume of adsorbate = 100 mL pH = 6.9

Time (min)	Absorbance and Conc. of Chromium metal ion solution at different temperature									
	306.5 k		**311.5 k**		**316.5 k**		**321.5 k**		**326.5 k**	
	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.
10	0.568	2.188	0.581	2.238	0.584	2.250	0.587	2.261	0.596	2.296
20	0.335	1.290	0.362	1.394	0.407	1.568	0.421	1.622	0.462	1.780
30	0.326	1.256	0.359	1.383	0.379	1.460	0.415	1.599	0.455	1.753
40	0.319	1.229	0.355	1.367	0.367	1.414	0.408	1.572	0.452	1.741
50	0.315	1.213	0.347	1.337	0.361	1.391	0.397	1.529	0.447	1.722
60	0.312	1.202	0.341	1.314	0.357	1.375	0.392	1.510	0.443	1.706
24 Hrs	0.272	1.048	0.305	1.175	0.321	1.237	0.343	1.321	0.376	1.448

3.3.5. Effect of pH: -

Table: 3.3.5. Absorbance and Concentration of Chromium [Cr (VI)] metal ion solution at different pH with time interval.

Amount of adsorbent = 1.0 g Conc. of adsorbate = 5 ppm.

Volume of adsorbate = 50 mL Temperature = 301.5±0.3 k

Sr. No.	pH	Absorbance and Conc. of Chromium metal ion solution at different pH.			
		30 min.		**24 Hrs.**	
		Absorbance	Concentration	Absorbance	Concentration
1	2	0.824	3.174	0.638	2.458
2	3	0.754	2.904	0.602	2.319
3	4	0.636	2.450	0.574	2.211
4	5	0.615	2.369	0.529	2.038
5	6	0.606	2.334	0.518	1.995
6	7	0.638	2.458	0.524	2.018
7	8	0.667	2.569	0.561	2.161
8	9	0.681	2.623	0.568	2.188
9	10	0.697	2.685	0.575	2.215
10	11	0.701	2.700	0.586	2.257

3.3.6. Effect of Zero Point pH: -

Table: 3.3.6. Effect of Zero Point pH at different initial pH

Amount of adsorbent = 0.02 g Conc. of adsorbate = 5 ppm.

Volume of adsorbate = 50 mL Temperature = 301.5±0.3 k

Initial pH	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00	11.00
pH after 24. Hrs.	2.397	3.357	4.311	5.308	6.222	6.895	7.752	8.653	9.606	10.607
ΔpH	-0.397	-0.357	-0.311	-0.308	-0.222	0.105	0.248	0.347	0.394	0.393

3.4. Adsorption Study of Copper [Cu (II)] Metal Ion on Sarpgandha *(Rauwolfia Serpentine) Leaves Powder (SLP) Low-Cost Adsorbent: -*

3.4.1. Effect of Contact time: -

Table: 3.4.1. Absorbance of Copper [Cu (II)] metal ions at different time interval

Amount of adsorbent = 1.0 g. Conc. of adsorbate = 100 ppm.

Volume of adsorbate = 100 mL pH = 6.1 Temperature = 300.2± 0.3 k.

Time (min.)	Absorbance and concentrations of Sarpgandha (Rauwolfia serpentine) adsorbent at different time interval.	
	[Cu (II)] metal ion	
	Absorbance	Concentration
10	0.828	36.316
20	0.701	30.746
30	0.673	29.518
40	0.657	28.816
50	0.649	28.465
60	0.645	28.289
24 Hrs.	0.555	24.342

3.4.2. Effect of Adsorbent Dose: -

Table: 3.4.2. Absorbance and Concentrations of Copper [Cu (II)] metal ion at different adsorbent dose of SLP with time interval

Conc. of adsorbate = 100 ppm. Temperature = 300.2±0.3 k.

Volume of adsorbate = 100 mL. pH = 6.1

Time (min.)	Absorbance and Conc. of Copper metal ions at different adsorbent dose.							
	0.5 g.		**1.0 g.**		**1.5 g.**		**2.0 g.**	
	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.
10	0.862	37.807	0.831	36.447	0.789	34.605	0.774	33.947
20	0.751	32.939	0.691	30.307	0.643	28.202	0.641	28.114
30	0.743	32.588	0.676	29.649	0.626	27.456	0.612	26.842
40	0.729	31.974	0.659	28.904	0.613	26.886	0.595	26.096
50	0.718	31.491	0.651	28.553	0.609	26.711	0.589	25.833
60	0.716	31.404	0.648	28.421	0.607	26.623	0.586	25.702
24 Hrs	0.655	28.728	0.329	14.430	0.214	9.386	0.158	6.9298

3.4.3. Effect of Initial Concentration:-

Table: 3.4.3. Absorbance and Conc. of Copper [Cu (II)] metal ion solution at different initial Conc. of solution with time interval.

Amount of adsorbent = 1.0 g. Temperature = 300.2±0.3 k.

Volume of adsorbate = 100 mL pH = 6.1

Time (min)	Absorbance and Conc. of Copper metal ion solution at different initial conc.							
	25 ppm		**50 ppm**		**75 ppm**		**100 ppm**	
	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.
10	0.214	9.386	0.436	19.123	0.675	29.605	0.914	40.088
20	0.178	7.807	0.368	16.14	0.566	24.825	0.797	34.956
30	0.167	7.3246	0.361	15.833	0.547	23.991	0.747	32.763
40	0.164	7.193	0.357	15.658	0.545	23.904	0.749	32.851
50	0.163	7.1491	0.354	15.526	0.542	23.772	0.742	32.544
60	0.162	7.1053	0.353	15.482	0.541	23.728	0.738	32.368
24 Hrs	0.129	5.6579	0.282	12.368	0.461	20.219	0.652	28.596

3.4.4. Effect of Temperature: -

Table: 3.4.4. Absorbance and Concentration of Copper [Cu (II)] metal ion solution at different temperature with time interval.

Amount of adsorbent = 1.0 g. Conc. of adsorbate = 100 ppm.

Volume of adsorbate = 100 mL. pH = 6.1

Time (min)	Absorbance and Concentration of Copper metal ion solution at different temperature									
	305.2 k		**310.2 k**		**315.2 k**		**320.2 k**		**325.2 k**	
	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.
10	0.937	41.096	0.973	42.675	1.011	44.342	1.097	48.114	1.114	48.860
20	0.803	35.219	0.825	36.184	0.852	37.368	0.915	40.132	0.946	41.491
30	0.786	34.474	0.806	35.351	0.846	37.105	0.892	39.123	0.931	40.833
40	0.767	33.640	0.789	34.605	0.832	36.491	0.868	38.070	0.924	40.526
50	0.754	33.07	0.781	34.254	0.827	36.272	0.859	37.675	0.919	40.307
60	0.751	32.939	0.779	34.167	0.825	36.184	0.856	37.544	0.917	40.219
24 Hrs	0.673	29.518	0.734	32.193	0.783	34.342	0.837	36.711	0.869	38.114

3.4.5. Effect of pH: -

Table: 3.4.5. Absorbance and Conc. of Copper [Cu (II)] metal ion different solution at pH with time interval.

Amount of adsorbent = 1.0 g. Conc. of adsorbate = 100 ppm.

Volume of adsorbate = 50 mL. Temperature = 302.5±0.3 k.

Sr. No.	pH	Absorbance and Conc. of Copper Cu (II) metal ion solution at different pH.			
		30 min.		**24 Hrs.**	
		Absorbance	Concentration	Absorbance	Concentration
1	2	0.573	25.132	0.535	23.465
2	3	0.535	23.465	0.519	22.763
3	4	0.518	22.719	0.482	21.140
4	5	0.507	22.237	0.467	20.482
5	6	0.496	21.754	0.435	19.079
6	7	0.511	22.412	0.457	20.044
7	8	0.533	23.377	0.474	20.789
8	9	0.554	24.298	0.481	21.096
9	10	0.596	26.140	0.496	21.754
10	11	0.607	26.623	0.503	22.061

3.4.6. Effect of Zero Point pH: -

Table: 3.4.6. Effect of Zero Point pH at different initial pH

Amount of adsorbent = 0.02 g. Conc. of adsorbate = 100 ppm.

Volume of adsorbate = 50 mL Temperature = 300.2±0.3 k

Initial pH	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00	11.00
pH after 24 Hrs.	2.181	3.138	4.139	5.143	6.136	6.122	7.937	8.872	9.856	10.857
ΔpH	-0.181	-0.138	-0.139	-0.143	-0.136	-0.122	0.063	0.128	0.144	0.143

4. Result and Discussion

4.1. Adsorption Study of Congo red (CR) on Sarpgandha (*Rauwolfia serpentine*) Leaves Powder (SLP) Low-Cost Materials: -

4.1.1. Introduction**:-**Adsorption is a surface phenomenon, which occurs due to active surface sites of adsorbents. There are different factors which describes the behavior of adsorbate towards adsorbents. In order to understand thoroughly adsorption process, and suitability of low-cost adsorbents for the removal of metal ions and organic dyes from aquatic systems, present investigation is under taken. Congo red (CR) (sodium salt of benzidinediazobis-1-naphthyl-amine-4sulphonic acid) is a benzidine-based azo dye and it was selected in this study as a model anionic dye and because of its complex chemical structure, solubility of in aqueous solution and its persistence, once it is discharged into natural environment. CR is metabolized to benzidine, a known human carcinogen and exposure to this dye can cause some allergic responses. CR mainly occurs in the effluents discharged from textile, paper printing, leather industries, etc. in waste waters [1-3]. Therefore, the removal of CR from wastewater effluents becomes environmentally important [4]. Several studies have shown that numerous materials have been applied in the removal of CR from aqueous solution, neem leaves [5], alternanthera bettzichiana plant [6], Rice hull ash [7], subabul seed pods [8], etc. The structure and some properties are already discussed in chapter No-I, section 1.1.1.

4.1.2. Effect of contact time**: -**All solutions were prepared in double distilled water, the concentration of CR was determined by using UV-Visible single beam Spectrophotometer, (Bio Era: Cal No.BI/CI/SP/SB-S-03) at λmax = 510 nm. The adsorption experiment was carried out in stirred batch process. For each experiment, 100 mL of CR dye solution of specified concentration was continuously stirred with 1.0 g. of Sarpgandha (*Rauwolfia serpentine*) leaves powder (SLP) adsorbent at room temperature, samples were withdrawn at appropriate time intervals and filtered the absorbance of supernant liquid was determined. The effect of contact time, effect of adsorbent dose, initial concentration, effect of temperature, effect of pH, effect of salt etc. were studied likewise.

Contact time is one of the important parameters for the assessment of practical application process, the effect of contact time was studied and maximum time was 60 minutes, at initial CR dye concentration 20 mg/L. The percentage adsorption of CR increased with increase in contact time, due to large surface area available of adsorbent [9]. The maximum percentage adsorption of CR was shown in Fig. 4.1.1.

4.1.3. *Effect of adsorbent dose*: - The adsorption of CR on Sarpgandha (*Rauwolfia serpentine*) leaves powder absorbent was studied by varying the Sarpgandha (*Rauwolfia serpentine*) leaves powder absorbents amount in the range of 0.5 to 2.5 g. in 100 mL adsorbate solution (Table: 3.1.2). The effect of adsorbent dose on the percentage adsorption of CR was presented in Fig.4.1.2. It is observed that the rate of percentage adsorption of CR increases with increase in adsorbent dose. This may be due to the fact that an adsorption is a surface phenomenon, the surface area of contact between adsorbent and adsorbate increases with increase in adsorbent dose.

***4.1.4. Effect of initial concentration*: -** The effect of initial concentration of CR on the rate of adsorption on adsorbents, the experiments were carried out at fixed adsorbent dose (1.0 gm.) at pH 6.4 with 100 ml of different initial concentration of CR (5-20 mg/L) at 24 hours.(Table: 3.1.3) from the Fig.4.1.3, it is evident that the percentage adsorption of CR decreases with increase in concentration of CR. At low concentration CR present in adsorption medium could interact with the binding sites on the surface of adsorbent so higher adsorption yields were obtained. At higher concentrations, lower adsorption yields were observed because of the saturation of the adsorption sites.

***4.1.5. Effect of temperature*: -**Temperature will be an important parameter affecting the adsorption processes. As the temperature increases, the rate of diffusion of adsorbate molecules across the external boundary layer and interval pores of the adsorbent particle increases. Changing to temperature will change the equilibrium capacity of the adsorbent for particulate adsorbate [10]. The experiments were performed using 20 mg/L. CR solution,1.0 g of adsorbents, at pH 6.4 for 24 hours at various temperatures 305.5, 310.5, 315.5, 321.5 and 325.5 k. (Table: 3.1.4)). The results were calculated and it suggests that percentage adsorption of CR decreases with increase in temperature.

***4.1.6. Effect of pH*: -**Adsorption experiments were carried out at pH 2.00 to 11.00. The acidic and alkaline pH of the media was maintained by adding the required amount of dilute HCl and NaOH solution [11]. Effect of initial pH was studied with blank CR solution of concentration 20 mg/L and pH of solution was kept 2.00 to 11.00 (Table: 3.1.6). As evident from (Fig.4.1.6.) with percentage adsorption of CR decreases with increase in pH, higher the percentage adsorption of CR was obtained at lower pH. At higher pH the high negatively charged adsorbents surface sites did not favor the adsorption of deprotonated CR due to electrostatic repulsion [12].

***4.1.7. Adsorption kinetics*: -** In this study batch adsorption kinetics of CR by all adsorbents have been studied in terms of pseudo first and pseudo second order kinetics. A straight line obtained for the plot of $log(q_e - q_t)$ against t, the pseudo first order rate constant (K_1), equilibrium adsorption density (q_e) and R^2 where calculated from the slope and intercept of this line. (Table: 4.1.1.) [13].

Table: 4.1.1. Kinetic parameter values with CR: -

Amount of adsorbent = 1.0 g. Conc. of adsorbate = 20 ppm.

Volume of adsorbate = 100 mL pH = 6.4 Temperature = 300.5±.3 K

Adsorbent	***Pseudo-First order***			***Second order***		
	K_1 (min^{-1})	***q_e (mg/g)***	***R^2***	***K_2 (g./mg.min)***	***q_e (mg/g)***	***R^2***
SLP	$1.241*10^{-2}$	387.035	0.753	$3.747*10^{-3}$	1405.97	0.998

The pseudo second order rate constant (K_2), (q_e) and R^2 were calculated from the intercept and slope of the plots of t/q_t against t.

The value of R^2 with first order was 0.753 and for second order R^2 value is 0.998. for Sarpgandha (*Rauwolfia serpentine*) adsorbent. It is clear that the adsorption of CR on all adsorbent was better represented by pseudo second order kinetics. This indicates that the adsorption system belongs to the second order kinetic model similar phenomenon were observed in the previous work [14, 15]

***4.1.8. Adsorption isotherm*:-**The Langmuir isotherm assumes that a monomolecular layer is formed when adsorption takes place and that there is no interaction between adsorbates which are adsorbed on adjacent binding sites. Therefore, both adsorption and desorption are independent of the total number of sites occupied. Adsorption and desorption are in dynamic equilibrium. It means the rate at which adsorbate are desorbed. Initially the rate of adsorption is fast since most of the binding sites on surface are freely available, whereas the rate of adsorption decreases when the surface of occupied with bound adsorbate. In other words, the rate of adsorption decreases with decreasing accessible surface area. The Langmuir model is seen to be satisfied due to the rearrangement of adsorption capacity and binding conformation. The isotherm parameters (Langmuir and Freundlich isotherm) were calculated. Amount of Congo red adsorbed (q_e), Langmuir constants (adsorption capacity(Q_0) and energy of adsorption *(b)* were obtained and calculate the separation factor (R_L) Table: 4.1.2.

Table: 4.1.2. Isotherm parameter values with CR:-

Conc. of adsorbate = 20 ppm. Volume of adsorbate = 100 mL

Temperature = 300.5±0.3 k pH = 6.4 Time = 24 hours.

Adsorbent	***Langmuir constants***				***Freundlich constants***		
	Q_0 (mg/g.)	***b (L/g.)***	***R_L***	***R^2***	***n***	***K_f (mg/g.(L/g.))$^{1/n}$***	***R^2***
SLP	4795.33	0.124	0.287	0.995	0.686	5.89	0.997

The R_L value was the 0.287. The Sarpgandha (*Rauwolfia serpentine*) adsorbent show $R_L$value 0.287. The *n* value was 0.686. The $R_L$value indicates the adsorption nature to be either unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if, $R_L = 0$ [16-21]. Since R_L values were found to be between 0 and 1 for CR studies, it is confirming that the ongoing adsorption of CR is favorable. The data reveal that the Freundlich model yields better fit than the Langmuir model. If value of $\frac{1}{n}$ is below one, it indicates a normal adsorption, on the other hand $\frac{1}{n}$ being above one indicates co-operative adsorption [22]. Since $\frac{1}{n}$ value was 0.686 indicates co-operative adsorption. The values of $\frac{1}{n}$ calculated and presented in Table: 4.1.2.

***4.1.2. Thermodynamics of adsorption*: -**Thermodynamic studies were performed to find the nature of adsorption process. Thermodynamic parameters such as Gibb's free energy change ΔG^0, enthalpy change ΔH^0 and entropy change ΔS^0 were calculated by using Van't Hoff's equation.

Table: 4.1.4. Thermodynamic parameter ΔG), ΔH° and ΔS° values with CR solution at different temperature: -.

Conc. of adsorbate = 20 ppm. Volume of adsorbate = 50 mL

Amount of adsorbent = 1.0 g pH = 6.283 Time = 24 hours.

Temp (K)	Free energy change (ΔG°), ΔH° and ΔS° values of CR solution at different temperatures		
	(ΔG°) KJ/mole.	−ΔH° KJ/mole	−ΔS° J/mole
305.5	-1.493	6.962	17.888
310.5	-1.404		
315.5	-1.314		
320.5	-1.225		
325.5	-1.135		

The Gibb's free energy change indicates the degree of spontaneity of the adsorption process. The negative value of ΔG^0 indicates that the adsorption is favorable and spontaneous [23, 24]. It has been reported that negative value of ΔG^0 (Table 4.1.4.) indicates that the adsorption is favorable and spontaneous.

The values of ΔH^0 and ΔS^0 were determined from the slopes and intercepts of the plot of $log\, K_c$ against $\frac{1}{T}$ respectively. The negative value of ΔH^0 suggests that the adsorption is exothermic [25, 26]. The positive value of ΔS^0suggests that the increased disorder and randomness at the solid solution interface with adsorption. It indicates that the negative value of ΔS^0 decreased disorder and randomness at the solid solution interface with adsorption.

4.1.3. Zero point pH: -

The pH point of zero charge (pHpzc) of the adsorbent is determined by powder addition method. 0.02 g adsorbent was added to 100 mL of conical flask containing 50 mL of CR solution containing 0.1 M NaCl solution. Several batches were carried out for, 2.00 to 11.00 initial solution pH, called pH_i. The pH was adjusted using 0.1 M HCl and0.1 M NaCl solution. The electrolyte solution with adsorbent was equilibrated for 24 h. After equilibrium, the final pH, $pH_f$was recorded. Both positive and negative ΔpH (pH_i - pH_f) values recorded for the adsorbent are plotted against the initial pH values. The pH at which ΔpHbecomes zero is called pH_{pzc}.The 6.0 to 6.5 range of zero-point charge was found in adsorbents used in present work. Cationic adsorption on any adsorbent will be favorable at pH> $pH_{pzc.}$ The surface of the adsorbent gets negatively charged and favors uptake of cationic dyes to increased electrostatic force of attraction. Thus, CR adsorption onto all use adsorbents was favored at higher pH.

The generalized surface group (SOH) shows two different dissociation reactions.

$$SOH + H \rightarrow SOH_2^+ \qquad K\alpha_1$$

$$SOH \rightarrow SO^- + H^+ \qquad K\alpha_2$$

Where, $K\alpha_1$ and $K\alpha_2$ are called intrinsic surface acidity constants.

When curves are plotted, the point of interaction with solution pH axis is called point of zero charge (pH_{pzc}). The pH_{pzc}values for modified and unmodified activated carbon are represented to be 7.07 and 6.54 [27].

4.2. Conclusion: -

The CR dye was adsorbed on agricultural solid low-cost adsorbent Sarpgandha (*Rauwolfia serpentine*) in batch adsorption technique. The effect of various operating conditions like contact time, adsorbent dose, initial CR concentration, temperature, initial pH of CR solution was investigated. The percentage adsorption efficiency of CR increased with increasing adsorbent dosage and contact time, while was decreased with increasing initial concentration, temperature and initial pH of CR solution. The CR adsorption equilibrium was attained after 24 hours.

The kinetics of adsorption of CR was studied by using pseudo first and pseudo second order kinetic equations for the experimental system; pseudo second order kinetic model provided the best correlation of the experimental data. The adsorption process follows by pseudo second order rate model better than a pseudo first order rate model. The negative value of ΔH^0 and ΔS^0 showed the adsorption is exothermic nature and a decrease in disorder of CR molecules in the adsorption process respectively. The R_L value showed that the adsorbents were favorable for the adsorption of CR. The results of investigation showed that Sarpgandha (*Rauwolfia serpentine*) adsorbent have considerable potential for the adsorption of CR from aqueous solution and may be used as a low cost natural and abundant source for the adsorption of CR and they may be alternative to more costly materials, It may also be effective in adsorbing as well as other harmful or undesirable species such as heavy metals, dyes, and other hazardous pollutants present in waste effluents. The result of this study indicates that Sarpgandha (*Rauwolfia serpentine*) adsorbent can be successfully used for the adsorption of CR from aqueous solution.

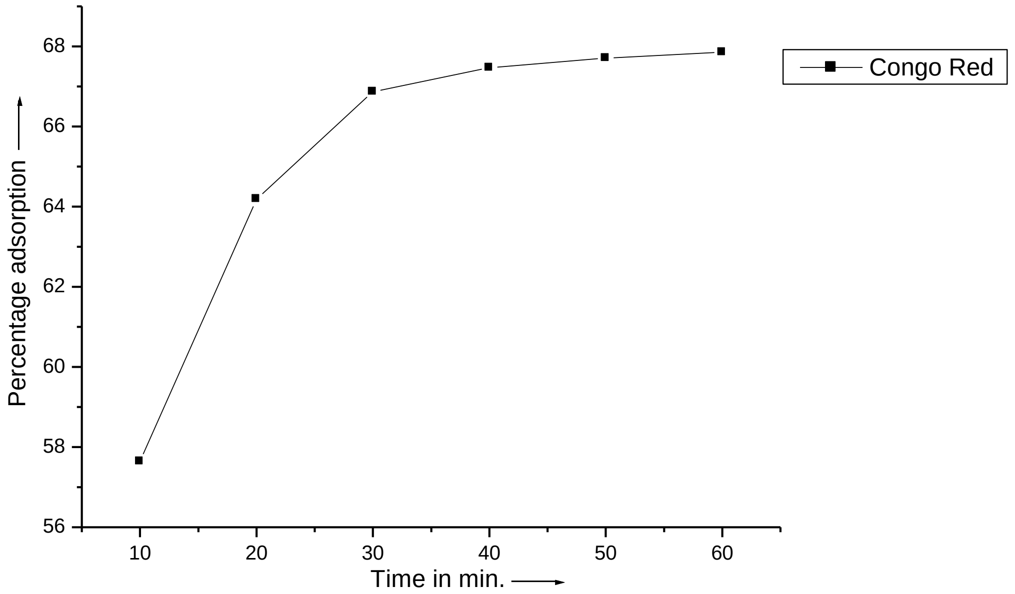

Fig.4.1.1: Effect of contact time on percentage adsorption of Congo red.
[Initial conc=20 ppm, Adsorbent dose=1.0 g, Volume of adsorbate=100 mL,Temp=300.5 k, pH=6.4]

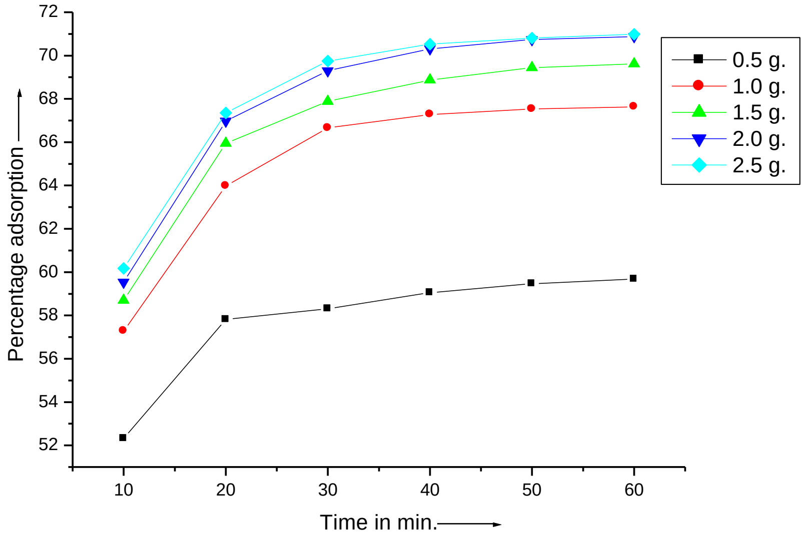

Fig.4.1.2: Effect of adsorbent dose on percentage adsorption of congo red due.
[Initial conc=20 ppm, Volume of adsorbate=100 mL, Temp=300.5 k, pH=6.4]

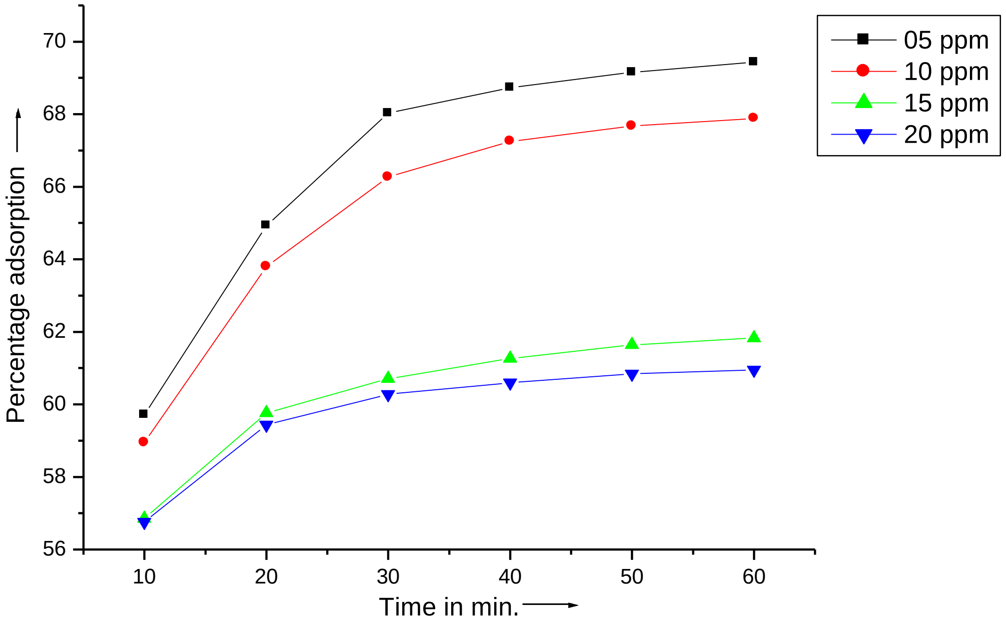

Fig.4.1.3.: Effect of initial concentration on percentage adsorption of congo red dye.
[Adsorbent dose=1.0 g, Volum of adsorbate=100 mL, Temp=300.5 k, pH=6.4]

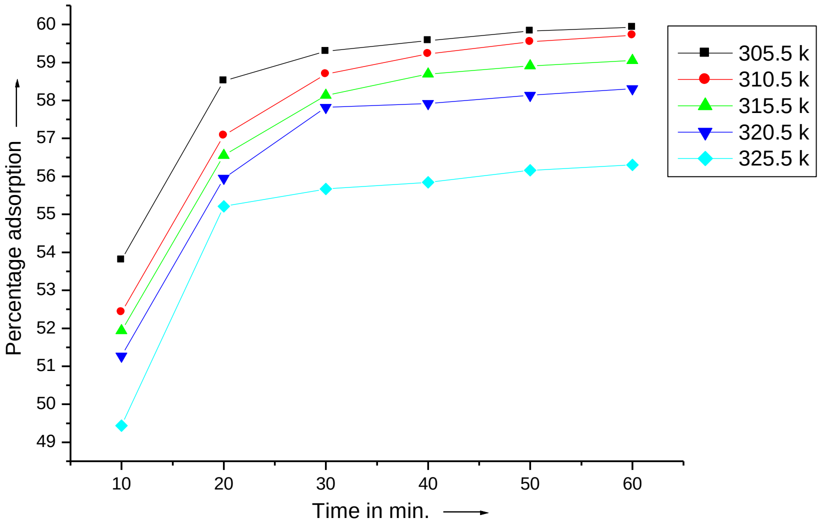

Fig.4.1.4: Effect of temperature on percentage adsorption of congo red dye.
[Initial conc.=20 ppm, Adsorbent dose=1.0 g, Volume of adsorbate=100 mL, pH=6.4]

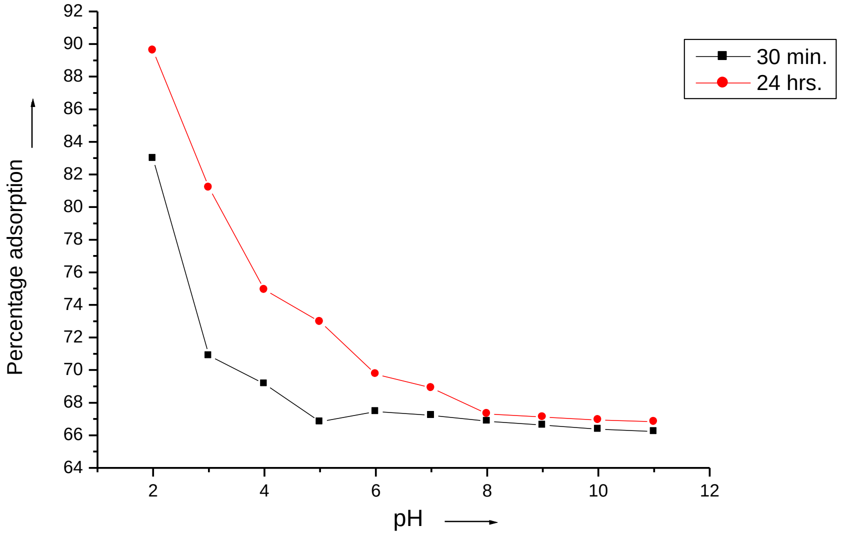

Fig.4.1.5: Effect of pH on percentage adsorption of congo red dye.

[Initial conc.20 ppm, Adsorbent dose=0.5 g,Volume of adsorbate=50 mL, Temp=300.5 k]

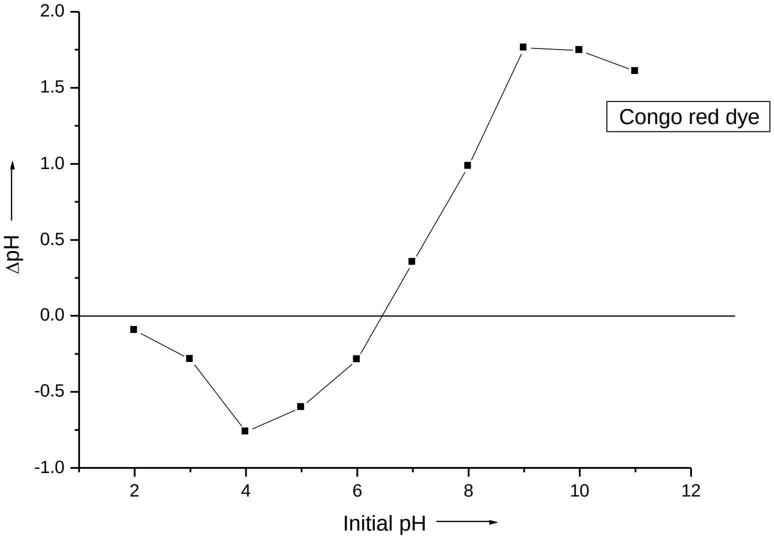

Fig.4.1.6: Effect zero point pH on percentage adsorption of congo red dye.

[Initial conc.=20 ppm, Adsorbent dose=0.02 g, Temp=300.5 k]

4.2. Adsorption Study of Methylene Blue (MB) on Sarpgandha (*Rauwolfia serpentine*) Leaves Powder (SLP) Low-Cost Materials: -

***4.2.1. Introduction*: -** Methylene blue (MB) has wider applications, which includes coloring papers, temporary hair colorant, dyeing cottons, wools and coating for paper stock [28]. MB causes some harmful effects such as eye injury for human and animals, vomiting, profuse sweating, diarrhea, gastritis, mental confusion, jaundice, and nausea in humans [29]. Previously several researchers had used several low-cost materials such a natural carbon nano tubes [30], tuberose sticks [31], water hyacinth root [32], guava seeds [33]. etc. as adsorbents.

4.2.2. Effect of contact time*: -** The agricultural materials like Sarpgandha **(Rauwolfia serpentine***)** has been used as a adsorbent for the removal of MB from its aqueous solutions. All solutions were prepared in double distilled water. For each experiment, 100 mL of MB dye solution was continuously stirred with 1.0 g. of adsorbent at room temperature, samples were withdrawn at appropriate time intervals and filtered the absorbance of supernant liquid was taken at λmax = 570 nm. The effect of contact time, effect of adsorbent dose, initial concentration, effect of temperature, effect of pH, etc. were studied likewise.

The effect of contact time on MB adsorption was shown (Table: 3.2.1.), the percentage adsorption of MB increasing with increasing in time and becomes constant after 60 minutes (Fig.4.2.1.) It is clear that the extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation is allowed. Hence at the beginning of adsorption, the driving force of different MB concentrations between solution and adsorbents were larger, so the adsorption rate was fast. The first phase was the instantaneous adsorption stage or external surface adsorption. Then the driving force becomes smaller and the adsorption rate was slower.

***4.2.3. Effect of adsorbent dose*: -**The adsorption of MB on all adsorbents was studied by varying the adsorbent dosage. The amount of MB adsorption increased with increase in dosage of adsorbent. Initially the rate of percentage adsorption of dye was found to increase rapidly with increase of adsorbent dose and slowed down latter, when the dose increased from 0.50 to 2.50 g. in each case. From the observation results, the optimum dose of adsorbent fixed for all adsorbents is 1.0 g. It can also be seen from Fig.4.2.2, which after dosage of 1.0 g. there was no significant changes in percentage adsorption of dye. Through the percentage adsorption increased with increased adsorption dosage. There are many factors which can contribute to this adsorption dose effect, (i) as the dosage of adsorption is increased, the adsorption sites remains unsaturated during the adsorption reaction leading to drop in adsorption capacity.(ii) The aggregation of sorbent particles at higher doses, which would lead to decrease in the surface area and a diffusional path length [34].

4.2.4. Effect of initial concentration*: -** Initial concentration has its own importance in adsorption process and variation in its concentration shows significant effect. The effect of initial concentration of MB on the extent of adsorption of MB dye in terms of percentage adsorption and the amount of MB adsorbed on prepared adsorbents viz. Sarpgandha **(Rauwolfia serpentine***)** leave powder (SLP) has been studied by varying the initial concentration of MB dye (25-100 mg/L) and keeping the other control parameters at their optimum conditions. The percentage adsorption of MB increases with decrease initial concentration. This is due to the fact that after the formation of mono layer at the lower initial concentration of methylene blue dye over the surface of adsorbent any further formation of layer of dye species is highly hindered. The variation can also be represented as in Fig.4.2.3 [35].

***4.2.5. Effect of temperature*: -**Temperature has important effect on adsorption was investigated in the temperature range of 305.9, 310.9, 315.9, 320.9., 325.9 k and 100 mg/L. (Table: 3.2.4). It was observed that adsorption decreases with increase in temperature (Figure 4.2.4). The solubility of the adsorbate increase in temperature, this affects work in the same direction, causing a decrease in adsorption ions or the mobility of the large MB increases with increase in temperature, which leads to a decrease in the adsorption capacity of composite with further increasing temperature, the same phenomenon was adsorbed by previous study [36, 37].

***4.2.6. Effect of pH*: -** pH is an important factor in controlling the adsorption of MB dye onto adsorbent. The adsorption of MB dye on Sarpgandha (*Rauwolfia serpentine*) leaves powder (SLP) was studied at a temperature of 300.9±0.3 K and 100 mg/L. concentration by varying the pH from 2.0 to 11.0, the solution was equilibrated for 24 hours. The results were shown in (Fig: 4.2.6.). The result indicates that the selected adsorbent showed good adsorption capacity in acidic medium than in basic medium. The percentage adsorption of MB dye of adsorption on SLP adsorbent progressively decreased on the pH of the solution increased from 2.00 to 11.0. At higher pH, the percentage adsorption was found to decrease because the surface area of the adsorbent was more protonated and competitive adsorption occurred between H^+ and free MB and their OH^- towards the fixation sites. Therefore, H^+ ions react with anionic functional groups on the surface of the adsorbent and results in restriction of the number of binding sites favorable for the adsorption of MB. The variation can also be represented as in Fig. 4.2.6.

***4.2.7. Adsorption kinetics*: -** The kinetics of adsorption was carried out to calculate the adsorption rate constants, the linear plot of $log(q_e - q_t)$ against t, and t/q_t against t were drawn for the first order and the second order models, respectively. The rate constants, the correlation coefficients (R^2) and calculated $\boldsymbol{R^2}$ for all adsorbents are in Table: 4.2.1.

Table: 4.2.1. Kinetic parameter values with MB: -

Amount of adsorbent = 1.0 g. Conc. of adsorbate = 100 ppm.
Volume of adsorbate = 100 mL. pH = 7.2 Temperature =300.9 ± 0.3 k

Adsorbent	***Pseudo-first order***			***Pseudo-second order***		
	K_1* *(min^{-1})	***q_e* *(mg/g.)***	***R^2***	***K_2* *(g./mg.min)***	***q_e* *(mg/g.)***	***R^2***
SLP	$2.998*10^{-2}$	1448.77	0.789	16167.51	$8122.95*10^{-4}$	0.999

The value of (R^2) with first order was 0.789. While for second order (R^2) value was 0.999 for SLP adsorbent. The values of (R^2) obtained from pseudo second-order model was higher than pseudo first-order model, indicating that the adsorption process followed the pseudo second-order model for entire adsorption period [38, 39].

4.2.8. Adsorption isotherm: - In this study, adsorption isotherms data was correlated using two well-known adsorption equations, Langmuir and Freundlich models [40].

The amount of MB adsorbed (q_e), Langmuir constants (capacity (Q_0) and energy (b) of adsorption) and Freundlich constants (adsorption capacity (K_f) and intensity (n) were shown in Table: 4.2.2.

Table: 4.2.2. Isotherm parameter values with MB: -

Conc. of adsorbate = 100 ppm. Volume of adsorbate = 100 ml.
Temperature = 309.4±0.3 K. pH = 7.2

Adsorbents	***Langmuir constants***				***Freundlich constants***		
	Q_0 (mg/g.)	**b (L/g.)**	**R_L**	**R^2**	**$\frac{1}{n}$**	**K_f (mg/g.(L/g.))$^{1/n}$**	**R^2**
SLP	20630.2	0.059	0.145	0.997	0.596	18.10	0.976

The R_L value was 0.145 for SLP adsorbent. The n value was for adsorbent 0.596 (Table 4.2.2.). The R_L Value indicates the adsorption nature to be either unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if, $R_L = 0$ [41-46]. Since R_L values lies between 0 to 1 for MB studies indicates that the adsorption of MB is favorable. The data reveal that the Langmuir model yields better fit than the Freundlich model. If value of $\frac{1}{n}$ is below one, it indicates a normal adsorption, on the other hand $\frac{1}{n}$ being above one indicates co-operative adsorption [47]. Since $\frac{1}{n}$ value was 6.419 indicates co-operative adsorption. The values of $\frac{1}{n}$ calculated and presented in Table: 4.1.2.

4.2.9. Thermodynamics of adsorption:- Thermodynamic parameters such as Gibb's free energy change (ΔG°) enthalpy change (ΔH°) and entropy change (ΔS^0) were calculated by using Van't Hoff's equation (Table: 4.2.3.), the (ΔG°) value of Sarpgandha **(***Rauwolfia serpentine***)** leaves powder (SLP) adsorbent was decreasing from 3.726 to 3.370 KJ/mole with increasing temperature. The negative value of (ΔG°) indicates that the adsorption of MB on adsorbent was thermodynamically favorable and spontaneous nature of adsorption and confirmed affinity of natural adsorbents for MB basic dye. The $(\Delta G°)$ value decreases with increase in temperature, it in Table: 4.2.3.

Table: 4.2.3. Free energy change $(\Delta G°)$, $\Delta H°$ and $\Delta S°$ values of MB solution different temperature: -

Conc. of adsorbate = 100 ppm. Volume of adsorbate = 100 mL
Amount of adsorbent = 1.0 g. pH = 7.2 Time = 24 hours.

Temp (K)	$\Delta G°$, $\Delta H°$ and $\Delta S°$ values of MB solution different temperature in KJ/mole		
	$\Delta G°$ KJ/mole	$-\Delta H°$ KJ/mole	$-\Delta S°$ J/mole
305.9	-3.726	9.171	17.821
310.9	-3.637		
315.9	-3.548		
320.9	-3.459		
325.9	-3.370		

It has been reported that $\Delta G°$ up to -20 KJ/mole are consistent with electrostatic interaction between sorption sites and the dye (physical adsorption), The $\Delta G°$ values obtained in this study for the MB are < -10 KJ/mole, which indicate that physical adsorption was the predominant mechanism in the adsorption process.

The negative values of $\Delta H°$ confirmed that the adsorption was exothermic in nature; it also explained that energy was liberated by the system during adsorption process, while the negative $\Delta H°$ values were suggested that there were no significant changes occurred in the internal structure of the adsorbent. Moreover, the values of $\Delta S°$ were less than 40 KJ/ mole, which indicated the physical adsorption [48, 49]. All these indicating that the process is slightly exothermic in nature. This is probably due to tendency of MB molecules to escape from the solid phase to bulk phase with an increase in temperature of the solution [50].

4.2.10. Zero point pH: -The pH point of zero charge (pH_{pzc}) of the adsorbent is determined by powder addition method. 0.02 g adsorbent was added to 100 mL of conical flask containing 50 mL of MB solution containing 0.1 M NaCl solution. Several batches were carried out for, 2.00 to 11.00 initial solution pH, called pH. The pH was adjusted using 0.1 M HCl and0.1 M NaCl solution. The electrolyte solution with adsorbent was equilibrated for 24 hours. After equilibrium, the final pH, pHf was recorded. Both positive and negative ΔpH (pH_i - pH_f) values recorded for the adsorbent are plotted against the initial pH values.The pH at whichΔpH becomes zero is called pH_{pzc}. At pH 6.7 zero-point charge was found in adsorbents used in present work. Cationic adsorption on any adsorbent will be favorable at pH > $pH_{pzc.}$ The surface of the adsorbent gets negatively charged and favors uptake of cationic dyes to increased electrostatic force of attraction. Thus, MB adsorption onto used adsorbent was favored at higher pH (pH>6.0) At lower pH ($pH<pH_{pzc}$), adsorbent surface is positively charged, concentrations of H^+ were high and they complete with positively charged MB cations for vacant adsorption sites causing a decrease in dye uptake. Similar trend was observed for adsorption of MB onto rice husk, [51] and wheat shells [52]. Present results are in good agreements with the above results.

4.2.11. Conclusion: -The adsorption of MB from aqueous solution using adsorbent like Sarpgandha **(***Rauwolfia serpentine***)** leaves powder (SLP) was investigated. Different important factors like contact time, adsorbent dose, initial concentration of MB, temperature, initial pH of solution and zero-point pH were optimized. The adsorption experiments show that the SLP low-cost adsorbent was very effective in adsorbing MB dye from aqueous solution, which were the percentage adsorption increased with the increase with the increase of contact time and achieves equilibrium at 24 hours. The MB dye adsorption was also influenced by dose of adsorbent and initial concentration of MB solution; it was increased with the increasing dose of adsorbent, while the percentage adsorption decreased with the increase in temperature and initial concentration of MB dye solution used. Equilibrium data very well fitted in a Langmuir isotherm model than Freundlich model confirming the adsorption capacity of MB onto adsorbent SLP with monolayer adsorption and intensity of adsorption, these isotherm models confirmed that adsorption of MB is favorable. The thermodynamic parameters such as Gibb's free energy change (ΔG°) enthalpy change *(*ΔH°*)* and entropy change (ΔS^0) studies indicates that, the negative values of *(*ΔH°*)* indicated the spontaneous nature of adsorption, physical adsorption and confirmed affinity of adsorbents for the MB basic dye. Negative value of ($\Delta \mathrm{S}^0$) confirmed the exothermic nature of the adsorption process. The values of R^2 obtained from pseudo-second order model were higher than pseudo-first order model for entire adsorption period. All investigation concludes that SLP adsorbent is very effective in adsorption of MB dye. Hence the study can be suggested as an alternative to adsorb MB dye from aqueous pollutants in standard conditions, and can be used for industrials for effluent treatments.

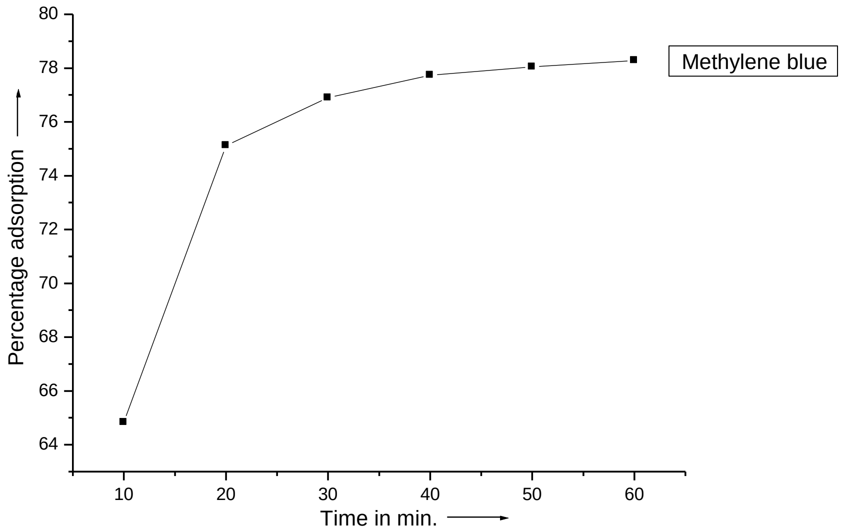

Fig.4.2.1: Effect of contact time on percentage adsorption of methylene blue dye.
[Initial conc=100 ppm,Adsorbent dose=1.0 g,Volume of adsorbate=100 mL, Temp=300.9 k, pH=7.2]

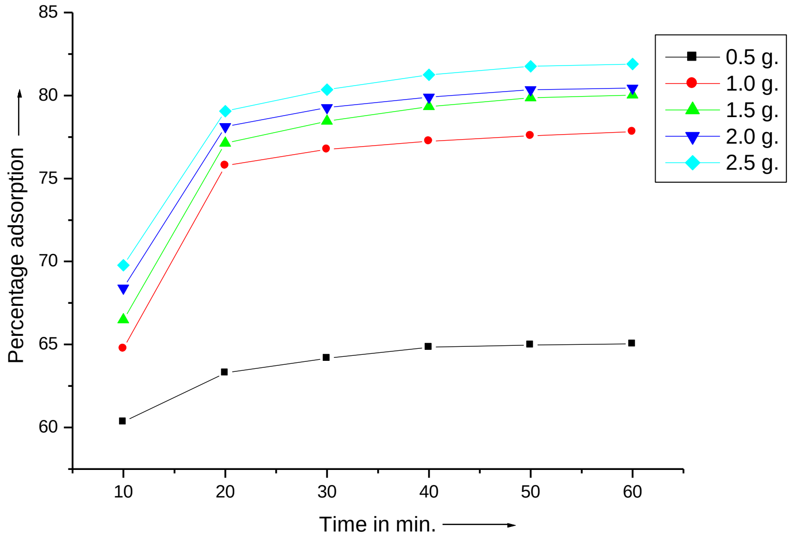

Fig.4.2.2.: Effect of adsorbent dose on percentage adsorption of methylene blue dye.
[Initial conc.=100 ppm, Volume of adsorbate=100 mL, Temp=300.9 k,pH=7.2]

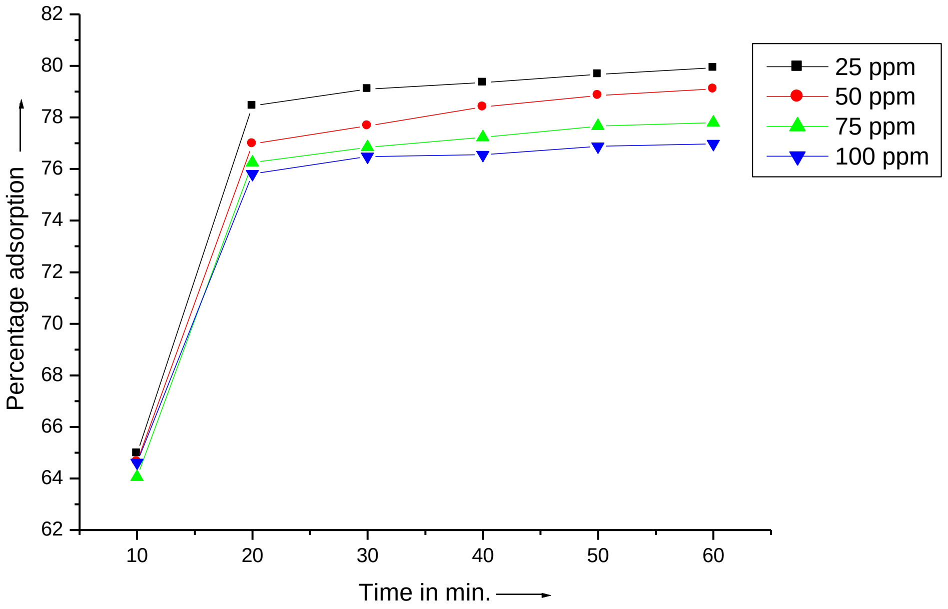

Fig.4.2.3: Effect of initial concentration of of adsorbate solution on percentage adsorption of methylene blue dye.
[Adsorbent dose=1.0 g, Volume of adsorbate=100 mL, Temp=300.9 k, pH=7.2]

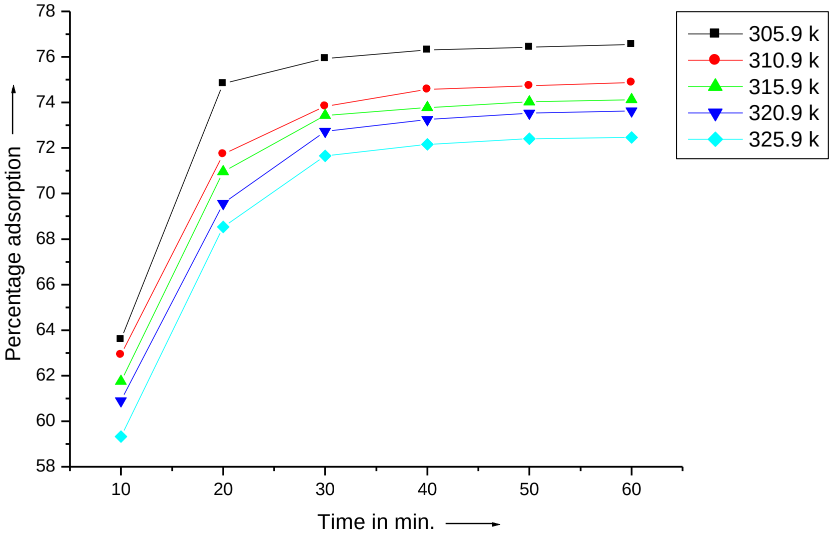

Fig.4.2.4.: Effect of temperature on percentage adsorption of methylene blue dye.
[Initial conc.=100 ppm, Adsorbent dose=1.0 g, Volume of adsorbate=100 mL, pH=7.2]

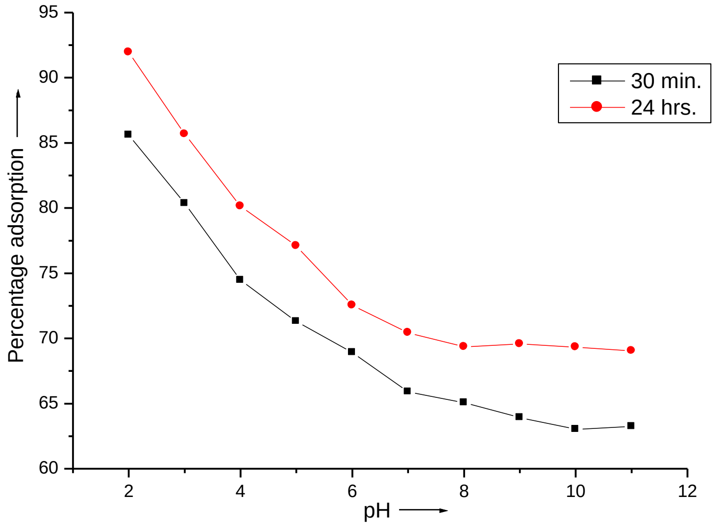

Fig.4.2.5.: Effect of pH on percentage adsorption of methylene blue dye.
[Initial conc.=100 ppm, Adsorbent dose=1.0 g, Volume of adsorbate=50 mL, temp=300.9 k]

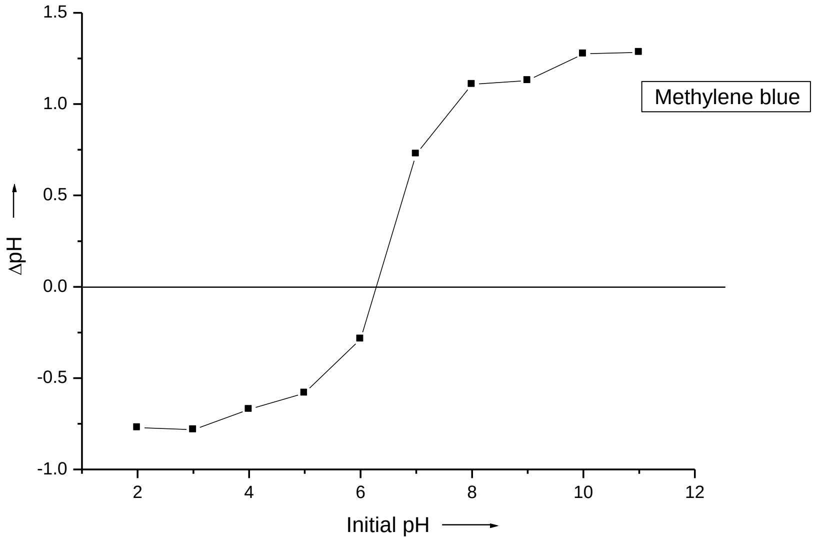

Fig. 4.2.6.: Effect of zero point pH on adsorption of methylene blue dye.
[Initial conc.=100 ppm, Adsorbent dose=0.02 g, Volume of adsorbate=50 mL, Temp=300.9 k]

4.3. Adsorption Study of Chromium [Cr (VI)] Metal Ions on Sarpgandha (*Rauwolfia serpentine*) Leaves Powder (SLP) Low-Cost Materials: -

4.3.1. Introduction: -Heavy metals like Cr, Pb, Ni, Cu, Hg, Cd etc. are common pollutants are spontaneously from different industrial, agricultural and domestic sources into the environment that causes a serious threat to the human as well as aquatic life. Cr is mainly used in a number of industrial applications including steel production, electroplating, leather tanning, nuclear power plant, textile industries, wood preservation, water-cooling, chromate preparation [53], manufacturing of dyes, paints, paper, battery, rubbers, petroleum refining processes [54] etc. Compared to other heavy metal ions Cr (VI) is abundant in nature, highly soluble and highly toxic as well as carcinogenic. Cr can cause human toxicity that includes lung cancer, as well as kidney, liver, and gastric damage [55]. The adsorption of Cr (VI) by a number of naturally available adsorbents like hazelnut shell [56], banana, orange peels [57], coffee beans [58], arjun nuts [59], archis hypogeal [60], sunflower stalks [61], maize bran [62], coconut shell, waste tea, rice straw, tree leaves and walnut husk [63] etc. had been used for the adsorption of Cr (VI).

4.3.2. Effect of contact time: -The low-cost adsorbents such as Sarpgandha **(***Rauwolfi* serpentine) leaves powder (SLP) have been used as a adsorbent for the removal of Cr (VI) metal ions from its aqueous solutions. All solutions were prepared in double distilled water. For each experiment, 100 mL of Cr (VI) solution was continuously stirred with 1.0 g. of adsorbent at room temperature, 10 ml of chromium sample solution was transferred to 100 mL standard flask; enough H_2SO_4 was added to make acid concentration 0.2 N on dilution up to 25 mL. Now add one ml of diphenyl carbazide [$(C_6H_5NH.NH_2)$ CO] solution, it was shacked till it got mixed with the solution, allow the solution to stand for 10 – 15 minutes. And samples were withdrawn at appropriate time intervals and filtered then absorbance of supernant liquid was taken at λmax = 540 nm. The effect of contact time, effect of adsorbent dose, initial concentration, effect of temperature, effect of pH, effect of salt etc. was studied likewise (The procedure and remaining detail are in Chapter II, the section 2.4.2.1.)

Contact time is one of the effective factors in batch adsorption process. In this stage, all of the parameters except contact time, including temperature (301.5±0.3k), adsorbent dose (0.5 g), initial concentration (5 mg/L), pH (6.9) was kept constants. The effect of contact time on Cr (VI) adsorption efficiency showed in Fig. 4.3.1. As it is shown, the percentage adsorption of Cr (VI) increased with increase with in contact time, due to large surface area available of adsorbent, percentage adsorption rate initially increased rapidly up to 60 minutes. Further increase in contact time did not increased percentage adsorption rapidly.

***4.3.3. Effect of adsorbent dose*: -** The effect of adsorbent dose on the adsorption was studied by varying the amount of adsorbent from 0.50 to 2.5 g. (Table: 4.3.2.). The adsorbent was added to 100 mL of Cr (VI) solution of 5 mg/L. concentration and equilibrated for 24 hours. After the equilibrium time, solution was analyzed for the amount of Cr (VI) and present adsorption was estimated. The effect of adsorbent dose on the adsorption of Cr (VI) by presented in Fig.4.3.2. It is evident from Fig.4.3.2. that percentage adsorption of Cr (VI) metal ion increases with increase in adsorbent dose, may be due to the increase in adsorbent surface area of adsorbent particles and the availability of more binding sites increases for adsorption [64].

***4.3.4. Effect of initial concentration*: -**Initial concentration is one of the effective factors on adsorption efficiency. The experiments were done with variable Cr (VI) initial concentration (5, 10, 15 and 20 mg/L) and at constant temperature (301.5±0.3 K.), pH (6.9±0.3), adsorbent dose (0.5 g/100 mL) and contact time (24 hours). The experimental results of the initial concentration of Cr (VI) on adsorption efficiency were shown in Fig.4.3.3. The Fig.4.3.3 indicates that, the chromium percentage adsorption efficiency decreased with the increase in initial concentration of Cr (VI) metal ion solution. In case of low Cr (VI) concentrations, the ratio of the initial number of the moles of chromium ions to the available surface area of adsorbent is large and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage adsorption of metal ions decreases with increase in concentration of adsorbate.

4.3.5. Effect of temperature: -Temperature is a significant parameter controlling adsorption of species in a system. This is also a fact that most adsorption processes are exothermic in nature and hence lower temperatures favor removal by adsorption [65]. Batch adsorption studies were carried out various temperatures 306.5, 311.5, 316.5, 321.5 and 326.5 K. (Table: 4.3.3.). In the present studies, percentage adsorption of Cr (VI) metal ions decreased with increase in temperature, this is due to escaping tendency of the adsorbate species from the surface of the adsorbent. The experimental results of the temperature on adsorption efficiency were presented in Fig.4.3.4. Effect of temperature was further studied in detail by calculating various thermodynamic parameters.

4.3.6. Effect of pH: - pH is an important controlling parameter in the adsorption process and the ionic form of the metal ion in solution. Adsorption experiments were carried out in the pH range 2.0 to 11.0, while keeping all other parameters constants. The pH of the chromium solution was adjusted after adding the adsorbent; the results are given in Fig. 4.3.4. It is observed that the adsorption of Cr (VI) was 53.31 % at optimum pH 6 after 30 min. and 60.09 % at 24 hrs. By increasing pH, decrease in adsorption percentage was observed. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent that ultimately lead to the reduction in sorption capacity [66]. As the maximum removal efficiencies for chromium observed in near neutral region, this study should be great advantage for the practical implementation of chromium removal from water and waste water.

4.3.7. Adsorption kinetics: -Kinetic model is helpful to understand the kinetic process of metal ions adsorption and to evaluate the performance of the adsorbents for metal removal. In order to investigate the adsorption of Cr (VI), different kinetic models were used to describe the rate of adsorbate uptake on the adsorbent.

Table: 4.3.1. Kinetic parameter values with Chromium [Cr (VI)] metal ion:-

Amount of adsorbent = 1.0 g. Conc. of adsorbate = 5 ppm.

Volume of adsorbate = 100 mL. pH = 6.9. Temperature = 301.5 ± 0.3 k.

Adsorbents	***Pseudo-first order***			***Pseudo-second order***		
	K_1 (min^{-1})	***q_t (mg/g.)***	***R^2***	***K_2 (g./mg.min)***	***q_t (mg/g.)***	***R^2***
SLP	$3.956*10^{-2}$	135.634	0.802	$4.475*10^{-4}$	414.94	0.995

In this study, pseudo first and pseudo second order kinetic models were applied to study the kinetics of the adsorption process and find the best fitted kinetic model for the experimental data. In pseudo first order kinetic model, the adsorption rate constant based on the adsorption capacity was determined by Lagergren equation [67]. A straight line for the plot of $\log(q_e - q_t)$ versus t, the pseudo first order rate constant (K_1), equilibrium adsorption density (q_e) and R^2.where calculated from the slope and interceptof this line. (Table: 4.3.1.) [68] The pseudo second order model is based on the assumption that the rate limiting factor may be chemisorptions involving valence forces through sharing of electrons between the adsorbents group and Cr (VI) ions, it predicted the behavior over the whole range of adsorption, the values of rate constant (K_2), (R_L) and R^2 were calculated from the intercept and slope of the plots of t/q_t against t .The values of R^2 with first order was 0.802, while for second order R^2 value is 0.995. It is clear that the adsorption of Cr (VI) on SLP adsorbent was better represented by pseudo second order kinetics. This indicates that the adsorption system belongs to the second order kinetic model similar phenomenon were observed in the previous work [69-71].

***4.3.8. Adsorption isotherms*: -** Classical adsorption models, such as the Langmuir and Freundlich models, have been extensively used to describe the equilibrium established between adsorbed Cr (VI) metal ions on the adsorbents and Cr metal ions remaining in the solution at a constant temperature. Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. However, the Freundlich model assumes that the uptake of metal ions occurs on a heterogeneous surface by monolayer adsorption [72]. The Langmuir isotherm constants, such as adsorption equilibrium *(b) (L/mg)*, and the saturated monolayer adsorption capacity *(Q_0) (mg/g)*, were calculated from the slop and intercept (plotting the graph between C_e/q_e *and* C_e) and to calculate the separation factor (R_L).The $R_L$value indicates the adsorption nature to be either unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if, $R_L = 0$.

Table: 4.3.2. Isotherm parameter values with Chromium [Cr (VI)] metal ions: -

Conc. of adsorbate = 5 ppm. Volume of adsorbate = 100 mL.
Temperature = 301.5 ±0.3 k. pH = 6.9 Time = 24 hours.

Adsorbent	***Langmuir constants***				***Freundlich constants***		
	Q_0 (mg/g.)	***b (L/g.)***	***R_L***	***R^2***	***$\frac{1}{n}$***	***K_f (mg/g.(L/g.))$^{1/n}$***	***R^2***
SLP	1385.44	0.148	0.575	0.999	7.86	1.811	0.999

The $R_L$value for SLP adsorbent was found to be 0.575 (Table 4.3.2.). Since$R_L$values obtained are $0 < R_L < 1$ indicates the favorable adsorption of Cr (VI) metal ions by SLP adsorbent under consideration. This means that the equilibrium isotherms can be well described by the Langmuir model, and the adsorption process is monolayer adsorption onto a surface with finite number of identical sites, which are homogeneously distributed over the adsorbent surface [73-77]. The Freundlich isotherm constants were the adsorption capacity *(K_f)* and adsorption intensity *(n)*. The values of n and K_f can be obtained from the slope and the intercept of the linear plot of $\log\frac{x}{m}$ against $\log C_e$ [78, 79]. If value of $\frac{1}{n}$ is below one, it indicates a normal adsorption, on the other hand $\frac{1}{n}$ being above one indicates co-operative adsorption. The values of $\frac{1}{n}$ greater than unity, that means adsorption is co-operative (Table: 4.3.2.).

4.3.9. Thermodynamics of adsorption: - Thermodynamic parameters such as Gibb's free energy change ΔG^0, enthalpy change $\Delta H^0$and entropy change ΔS^0 were calculated at different temperatures usin Van't Hoff's equation (Table: 4.3.3.).

Table: 4.3.3. Free energy change *($\Delta G°$)*, ΔH^0 and ΔS^0 of Chromium [Cr (VI)] metal ion solution at different temperature: -

Conc. of adsorbate = 5 ppm. Volume of adsorbate = 100 mL.
Amount of adsorbent = 1.0 g. pH = 6.9 Time = 24 hours.

Temp (k)	Free energy change ($\Delta G°$), ($\Delta H°$) and ($\Delta S°$) of Chromium [Cr (VI)] metal ion solution at different temperature.		
	$-\Delta G°$ KJ/mole	$-\Delta H°$ KJ/mole	$-\Delta S°$ J/mole
306.5	3.363	16.941	44.00
311.5	3.141		
316.5	2.920		
321.5	2.698		
326.5	2.477		

It has been reported that ΔG^0 up to -20 KJ/mole are consistent with electrostatic interaction between sorption sites and the metal ion (physical adsorption), while ΔG^0 values more negative than -40 KJ/mole involve charge sharing or transfer from the adsorbent surface to the metal ion to form a co-ordinate bond (chemical adsorption). TheΔG^0 values obtained in this study for the Cr (VI) metal ions are < -10 KJ/mole, which indicate that physical adsorption (Table 4.3.3.), was the predominant mechanism in the adsorption process. The negative value of ΔG^0 indicates that the adsorption is favorable and spontaneous at higher temperature [80, 81]. The value of ΔH^0 was for adsorbent is -16.941 KJ/mole. The negative value of ΔH^0suggests that the adsorption is exothermic. The values of ΔS^0 was for adsorbent is 0.044 KJ/mole. The negative value of ΔS^0 suggests that the decreased disorder and randomness at the solid solution interface with adsorption.

4.3.10. Zero point pH: -The pH point of zero charge (pH_{pzc}) of the adsorbent is determined by powder addition method. 0.02 g adsorbent was added to 50 ml of conical flask containing 20 mL of Cr (VI) metal ion solution containing 0.1 M NaCl solution. Several batches were carried out for, 2.00 to 11.00 initial solution pH, called pH_i. The pH was adjusted using 0.1 M HCl and0.1 M NaCl solution. The electrolyte solution with adsorbent was equilibrated for 24 hours. After equilibrium, the final pH, pH_f was recorded. Both positive and negative ΔpH (pH_i - pH_f) values recorded for the adsorbent are plotted against the initial pH values. The pH at which ΔpH becomes zero, is called pH_{pzc}. The 6.7 is a zero-point charge found in adsorbents used in present work. Cationic adsorption on any adsorbent will be favorable at $pH > pH_{pzc.}$ The surface of the adsorbent gets negatively charged and favors uptake of cationic dyes to increased electrostatic force of attraction. The generalized surface group (SOH) shows two different dissociation reactions.

$$SOH + H \rightarrow SOH_2^+ \qquad K\alpha_1$$

$$SOH \rightarrow SO^- + H^+ \qquad K\alpha_2$$

Where, K_1 and K_2 are called intrinsic surface acidity constants.

When curves are plotted, the point of interaction with solution pH axis is called point of zero charge (pH_{pzc}).

4.3.11. *Conclusion*:-The main goal of present work is to develop low cost Sarpgandha **(***Rauwolfi* serpentine) leaves powder (SLP) for the Cr (VI) adsorption in aqueous media; the high capacities of the adsorbents to adsorb Cr (VI) had been demonstrated, the adsorption of Cr (VI) from aqueous solution using SLP was investigated. The statistical parameter indicated that the adsorption of Cr (VI) onto natural adsorbents follow pseudo–second order model. By studies the effect of dose, equilibrium isotherm data was better fitted using Langmuir isotherm model than Freundlich isotherm model, which was in good agreement with the experimental data. Adsorption of Cr (VI) was found to increase with increase in time and adsorbent dose while adsorption decreases with increase in initial concentration as well as temperature. The adsorption of Cr (VI) initially increases with increase in pH up to pH= 6; then adsorption of Cr (VI) decreases. The values of $\Delta G°, \Delta H°, and\ \Delta S°$ were negative confirmed the spontaneous and exothermic nature of the adsorption process. The present investigation showed that SLP can be used as potential low-cost adsorbents for the adsorption of Cr (VI) from aqueous solutions over a wide range of concentrations. The SLP adsorbent has been proved as one of the efficient adsorbents for the adsorption of Cr (VI) from industrial wastewater.

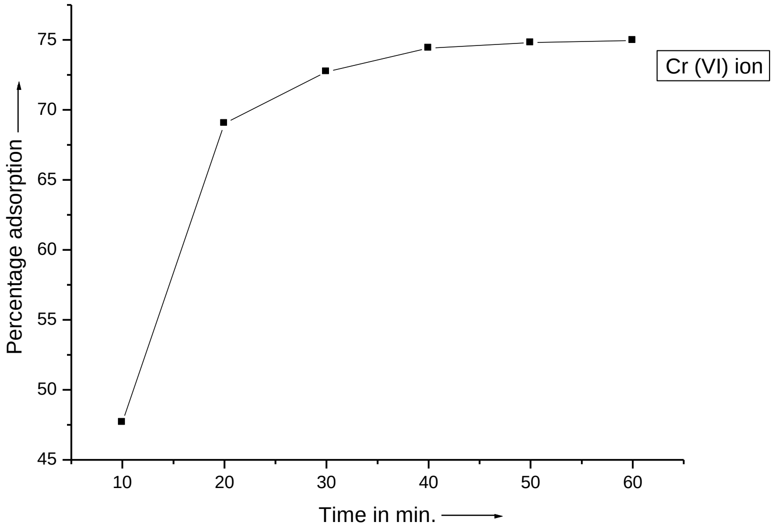

Fig.4.3.1.: Effect of contact time on percentage adsorption of Cr (VI) metal ion.
[Initial conc.=5 ppm, Adsorbent dose=1.0 g, Volume of adsorbate=100 mL, Temp=301.5 k, pH=6.9]

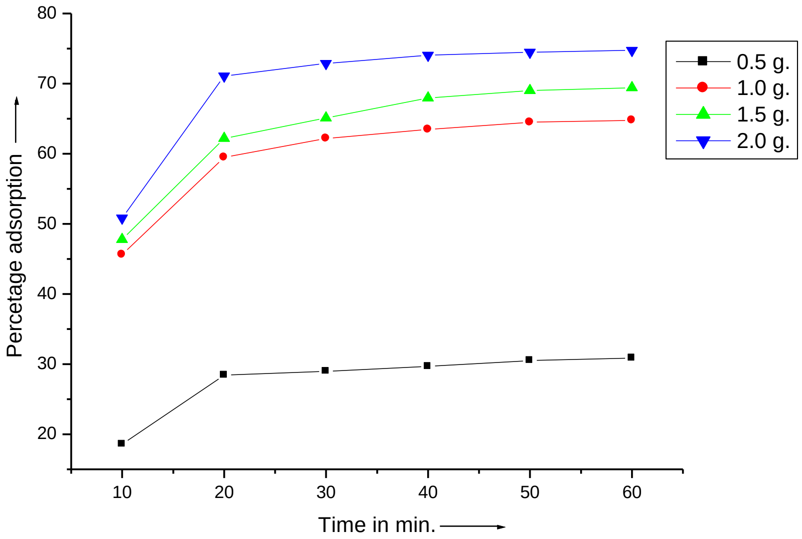

Fig.4.3.2.: Effect of adsorbent dose on percentage adsorption of Cr (VI) metal ion.
[Initial conc.=10 ppm, Volume of adsorbate=100 mL, Temp=301.5, pH=6.9]

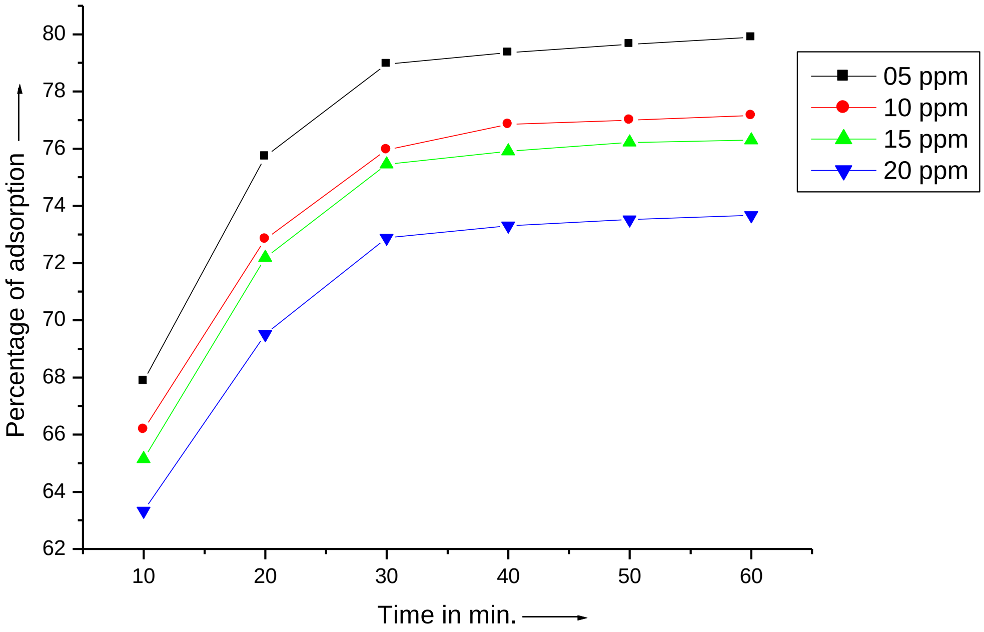

Fig.4.2.3.: Effect of initial concentration of adsorbate on percentage adsorption of Cr (VI) metal ion.
[Adsorbent dose=1.0 g,volume of adsoebate=100 mL,temp=301.8 k, pH=6.9]

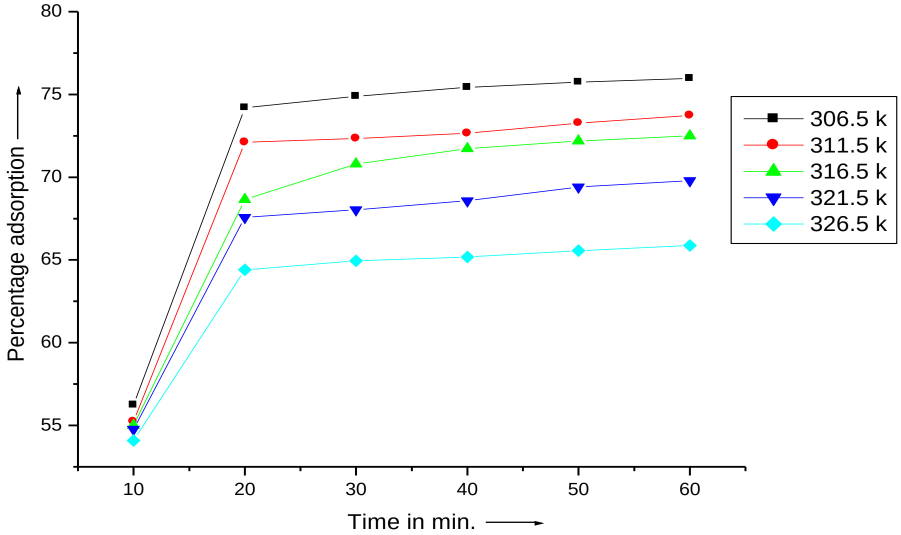

Fig.4.3.4.: Effect of temperature on percentage adsorption of Cr (VI) metal ion.
[Initial conc.=5 ppm,Adsorbent dose=1.0 g,Volume of adsorbate=100 mL,pH=6.9]

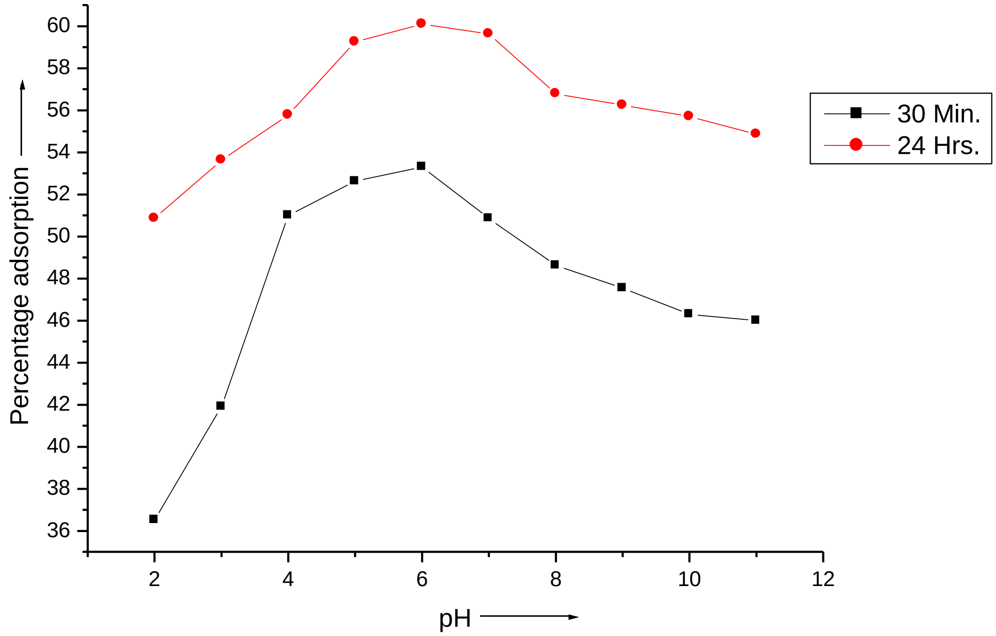

Fig.4.3.5.: Effect of pH on percentage adsorption of Cr (VI) metal ion.
[Initial conc.= 5 ppm, Adsorbent dose=0.5 g, Volume of adsorbate=50 mL, Temp=301.5 k]

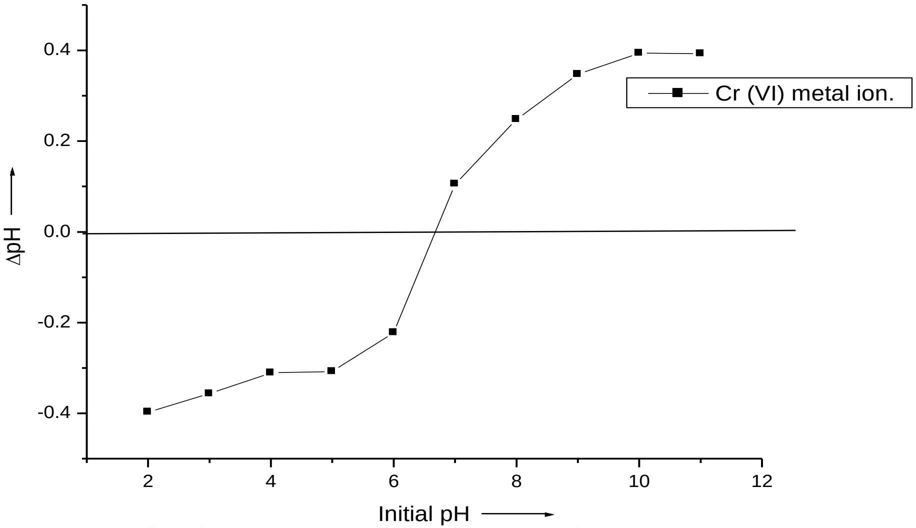

Fig.4.3.6.: Effect of zero point pH on percentage adsorption of Cr (VI) metal ion.
[Initial conc.=5 ppm, Adsorbent dose=0.02 g, Volume of adsorbate=50 mL, Temp=301.5 k]

4.4. Adsorption Study of Copper [Cu (II)] Metal Ions on Low-Cos Sarpgandha (*Rauwolfi* serpentine) Leaves Powder (SLP) Adsorbent: -

4.4.1. Introduction: - Copper is considered as micronutrient but is extremely toxic to living organisms at higher concentrations. The main source of copper pollution are metal cleaning and plating baths, paints and pigments, a pulp, paper, board, mills, wood pulp production and the fertilizer industry [82, 83]. Copper may also be found as a contaminant on food, especially shellfish, liver, mushrooms, nuts and chocolate. The World Health Organization (WHO) recommends a maximum acceptable concentration of Cu (II) as 1.5 mg/L. in drinking water. It is a transition metal, has three common oxidation, Cu (0) (metal), Cu (I) (cuprous) and Cu (II) (cupric), the main species of concern in aqueous solution is Cu (II) [84], It is an essential element for human beings and body can regulate its level home statistically but large doses can be harmful. Some evidences are here suggesting carcinogenic nature of copper, it has been reported that excessive intake of copper by humans leads to hepatic and renal damage, capillary damage, gastrointestinal irritation, nausea, headache, respiratory difficulty, central nervous system irritation, lungs cancer, liver and kidney failure and even death [85]. Copper has damaged the marine ecosystem and damaged gills, liver, kidneys, the nervous system and changing sexual life of fishes [86, 87]. Therefore, removal of copper from effluents is essential not only to protect the water resources but also to slow down the fast depletion of copper sources. The number of materials was developed for the removal of the metals like Cu (II) from industrial effluents using different adsorbents such as rice husk [88], sawdust [89], wheat shell [90], cashew nut shell [91], tea leaves [92], seed and seed shell of mango [93] etc.

4.4.2. Effect of contact time*: -** The adsorption experiments were carried out in stirred batch mode to perform the experiment, working solution of Cu (II) was prepared by dissolving the respective metal sulfate in double distilled water, the Sarpgandha **(Rauwolfi* serpentine) leaves powder was used as adsorbent for adsorption of Cu (II) metal ions. The residue was withdrawn at appropriate time intervals and filtered; the absorbance of supernant liquid was determined at λmax = 560 nm. The effect of contact time, effect of adsorbent dose, initial concentration, effect of temperature and effect of pH etc. were studied likewise (See Chapter II, section 2.4.2.2.)

Effect of contact time is an important factor affecting adsorption. On exposing the adsorbate solution to the adsorbent for varying length of time, the percentage adsorption of Cu (II) onto adsorbents increased with increasing time of contact in the initial stage, due to large surface area available of adsorbent. The maximum percentage adsorption of Cu (II) was 71.71 while minimum percentage adsorption of Cu (II) 63.68 on adsorbent after 60 minutes as presented in Fig. 4.4.1.

***4.4.3. Effect of adsorbent dose*: -** The adsorbent dose is another important parameter, which affects the extent of Cu (II) metal uptake from the solution, the adsorption of Cu (II) metal ion on adsorbent was studied at temperature 300.2±0.3 k. and pH = 6.1 by varying the adsorbent dose 0.5 to 2.5 g/100 mL adsorbate solution at 100 mg/L. Cu (II) metal ion concentration. The percentage adsorption of Cu (II) ion increases with increase in adsorbent dose due to the increase in active sites on the adsorbent and thus making easier penetration of the Cu metal ions to the adsorption sites as presented in Fig. 4.4.2.

***4.4.4. Effect of initial concentration*: -** In batch adsorption process the initial metal Ion concentration of Cu (II) metal ion in the solution plays key role as a driving force to overcome the mass transfer resistance between the solution and solid phase. The effect of initial Cu (II) metal ion concentration ranging from 25 to 100 mg/L. on adsorbents was studied by taking different concentration of $CuSO_4$ solutions at pH 5.3±0.3, while keeping the dosage of the adsorbent 0.5g./100mL constant and temperature 300.2±0.5 k. The results are shown in Fig. 4.4.3. The percentage adsorption of Cu (II) metal ion decreases with increase in concentration of Cu metal ion solution on SLP adsorbent.

***4.4.5. Effect of temperature*: -** The adsorption of Cu (II) ion at different temperatures namely 305.2, 310.2, 315.2, 320.2 and 325.2 k. were studied. The percentage adsorption of Cu (II) was found to decreases with increase in temperature as shown in Fig.4.4.5. It reveals that the adsorbate-adsorbent system is exothermic in nature for which the evaluation of thermodynamic parameters was carried out.

***4.4.6. Effect of pH*: -** The pH value of aqueous solution is an important parameter in adsorption process because it affects the surface charge of the adsorbent, the degree of ionization and specification of the adsorbate [94]. The batch equilibrium studied at 100 mg/L. of Cu (II) concentration with different pH values ranging from 2.00 to 11.0 as shown in Fig.4.4.6. Percentage adsorption of Cu (II) metal ion increased with increase of pH from 2.00 to 6.0 then percentage adsorption decreases with increase in pH. The lower the pH, the more H^+ ions competing with Cu (II) ions for adsorbent sites inhibiting Cu (II) adsorption. However, as pH increases, surface H^+ ions are replaced by OH^- ions increasing negative surface charge favorable to cationic adsorption and result in increased Cu (II) uptake by the adsorbent, which explains the obtained results in Fig.4.4.6.

***4.4.7. Adsorption kinetics*: -** In order to examine the controlling mechanism of adsorption process such as mass transfer and chemical reaction, the pseudo first and pseudo second order kinetic equations were used to test the experimental data. In pseudo first order kinetics, the straight line of plotted $\log(q_e - q_t)$ against t, were used to calculate the pseudo first order rate constant (K_1), equilibrium adsorption density (q_e) and R^2.

Table: 4.4.1. Kinetic parameter values with Copper [Cu (II)] metal ion: -

Amount of adsorbent = 1.0 g. Conc. of adsorbate = 100 ppm.

Volume of adsorbate = 100 mL pH = 6.1 Temperature = 300.2 ± 0.3 k

Adsorbent	***Pseudo-first order***			***Pseudo-second order***		
	K_1 (min^{-1})	***q_e (mg/g.)***	***R^2***	***K_2 (g/mg.min)***	***q_e (mg/g.)***	***R^2***
SLP	$2.00*10^{-2}$	1117.172	0.810	$1.011*10^{-4}$	7345.00	0.999

In pseudo second order kinetics, the straight line of plotted t/q_t against t , has been tested the rate constant $(K_2), (q_e)$ and R^2 from the intercept and slope of the plots. It suggests the applicability of this kinetic model to fit the experimental data. The value of R^2 with first order was 0.810. For second order R^2 values are 0.999 for SLP adsorbent. It is clear that the adsorption of Cu (II) on SLP adsorbent was better represented by pseudo second order kinetics as presented in Table: 4.4.1. This indicates that the adsorption system belongs to the second order kinetic. It is more likely to predict that the adsorption behavior may involve valiancy forces through sharing of electrons between transition metal cations and adsorbent [95-97].

4.4.8. Adsorption isotherm*: -** The essential features of a Langmuir isotherm can be expressed in terms of dimensionless constant or separation factor R_L. The amount of Cu (II) metal ion adsorbed (q_e), Langmuir constants (capacity (Q_0) and energy (b) of adsorption). The R_L value was for Sarpgandha **(Rauwolfi* serpentine) adsorbent was found to be same (0.999). The Freundlich constants (adsorption capacity (K_f) and intensity (n)) were calculated from the slope and intercept of the plots *Log (x/m)* versus *Log* C_e. The n values were for adsorbents from 1.111 to 1.002. (Table: 4.4.2.). The R_L value indicates the adsorption nature to be either unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if, $R_L = 0$ [98-103].

Table: 4.4.2. Isotherm parameter values with Copper [Cu (II)] metal ions: -

Conc. of adsorbate = 100 ppm. Volume of adsorbate = 100 mL
Temperature = 300.2±0.3 k. pH = 6.1 Time = 24 hours.

Adsorbent	***Langmuir constants***				***Freundlich constants***		
	Q_0 (mg/g)	***b (L/g)***	***R_L***	***R^2***	$\frac{1}{n}$	***K_f (mg/g(L/g))$^{1/n}$***	***R^2***
SLP	41641.51	0.018	0.356	0.999	0.784	10.347	0.999

Since $\boldsymbol{R_L}$ values lie between 0 to 1 for Cu (II) metal ion studies indicate that the adsorption of Cu (II) metal ion is favorable. The data reveal that the Langmuir model as well as Freundlich model better fits. If value of $\frac{1}{n}$ is below one, it indicates a normal adsorption, on the other hand $\frac{1}{n}$ being above one indicates co-operative adsorption. The values of $\frac{1}{n}$ greater than unity, that means adsorption is co-operative (Table: 4.4.2.). The result indicates that the adsorption of Cu (II) metal ion was best fitted Langmuir adsorption isotherm model than Freundlich.

***4.4.9. Thermodynamics of adsorption*: -** The thermodynamic parameters viz. Gibb's free energy change ΔG^0, enthalpy change ΔH^0 and entropy change ΔS^0 were calculated at different temperatures by using Van't Hoff's equation (Table 4.4.3.). The values of ΔH^0 and ΔS^0 were determined from the slopes and intercepts of the plot of $\log K_c$ against $\frac{1}{T}$ respectively.

Table: 4.4.3. Free energy change ($\Delta G°$), ($\Delta H°$) and ($\Delta S°$) of Copper [Cu (II)] metal ion solution at different temperature: -

Conc. of adsorbate = 100 ppm. Volume of adsorbate = 100 mL.

Amount of adsorbent = 1.0 g. pH = 6.1 Time = 24 hours.

Temp (k)	Free energy change ($\Delta G°$), ($\Delta H°$) and ($\Delta S°$) of Copper [Cu (II)] metal ion solution at different temperature		
	$-\Delta G°$ KJ/mole	$-\Delta H°$ KJ/mole	$-\Delta S°$ J/mole
305.2	2.180	16.067	45.523
310.2	1.953		
315.2	1.725		
320.2	1.498		
325.2	1.270		

The negative value of ΔG^0 (Table: 4.4.3.) confirms that the feasibility of the reaction and spontaneous nature of the adsorption [104, 105]. It has been reported that ΔG^0 up to -20 KJ/mole are consistent with electrostatic interaction between sorption sites and the metal ion (physical adsorption), while ΔG^0 values more negative than -40 KJ/mole involve charge sharing or transfer from the adsorbent surface to the metal ion to form a co-ordinate bond (chemical adsorption). The ΔG^0 values obtained in this study for the Cu (II) metal ions are < -10 KJ/mole, which indicate that physical adsorption was the predominant mechanism in the adsorption process. The negative value of ΔH^0 suggests that the adsorption to be in agreement with the exothermic nature of interaction. [106,107]. The negative value of ΔS^0 suggests that the decreased disorder and randomness at the solid solution interface with adsorbent while the adsorption there are some structural changes in the Cu (II) ion and the adsorbent occurs.

4.4.10. Zero point pH: - The pH point of zero charge (pH_{pzc}) of the adsorbent is determined by powder addition method. 0.02 g adsorbent was added to 50 mL of conical flask containing 20 mL of Cu (II) metal ion solution containing 0.1 M NaCl solution. Several batches were carried out for, 2.00 to 11.00 initial solution pH, called pH. The pH was adjusted using 0.1 M HCl and 0.1 M NaCl solution. The electrolyte solution with adsorbent was equilibrated for 24 hours. After equilibrium, the final pH, pH_f was recorded. Both positive and negative ΔpH (pH_i - pH_f) values recorded for the adsorbent are plotted against the initial pH values. The pH at which ΔpH becomes zero is called pH_{pzc}. The 7.0 of zero-point charge was found in adsorbent used in present work. Cationic adsorption on any adsorbent will be favorable at $pH > pH_{pzc.}$ The surface of the adsorbent gets negatively charged and favors uptake of cationic Cu (II) metal ion to increased electrostatic force of attraction. Thus, Cu (II) metal ion adsorption onto all used adsorbents are favored at higher pH (pH >7.0) At lower pH ($pH<pH_{pzc}$), adsorbent surface is positively charged, concentrations of H^+ were high and they complete with positively charged Cu (II) metal ion for vacant adsorption sites causing a decrease in Cu (II) metal ion uptake.

4.4.11. Conclusions: - Adsorption is a strong choice for the adsorption of Cu (II) metal asit is operationally simple and can adapt to change wastewater flow rates and compositions. The Cu (II) metal ion was adsorbed on agricultural solid low-cost adsorbent Sarpgandha **(***Rauwolfi* serpentine) leaves powder (SLP) in batch adsorption technique. The effect of various factors like contact time, adsorbent dose, initial concentration of Cu (II) metal ion, temperature and initial pH of Cu (II) metal ion solution were investigated. The percentage adsorption of Cu (II) metal ion was increased with contact time, adsorbent dose as well as initial pH of metal ion solution, while percentage adsorption decreased with increase in temperature as well as initial concentration of Cu (II) metal ion solution. Experiments were investigating that the adsorption process followed the pseudo second order model for entire adsorption period because the values of R^2 obtained from pseudo second order model were higher than the pseudo first order model. This work clearly indicates the potential of using SLP adsorbent is excellent adsorbent for the adsorption of Cu (II) metal ions and would be useful for the design of wastewater treatment plants for heavy metal ions. The equilibrium data was analyzed for the Langmuir and Freundlich adsorption isotherm models. Among these two isotherms, Langmuir isotherm model fitted well with the experimental data than Freundlich isotherm. This confirms the monolayer adsorption process. The percentage adsorption decreased with increasing the temperature, the results were used to calculate the thermodynamic parameters, the negative value of ΔH^0 and ΔS^0showed the adsorption is spontaneous and exothermic nature. The negative values of ΔG^0 indicated the spontaneous nature of adsorption, physical adsorption and confirmed affinity of adsorbents for the Cu (II) metal ions. The results confirmed that SLP adsorbent is illustrated higher adsorption capacities and can be used for the adsorptive removal of Cu (II) metal ions from different aqueous solutions, and its excellent adsorption behaviors for other metal ions can be expected.

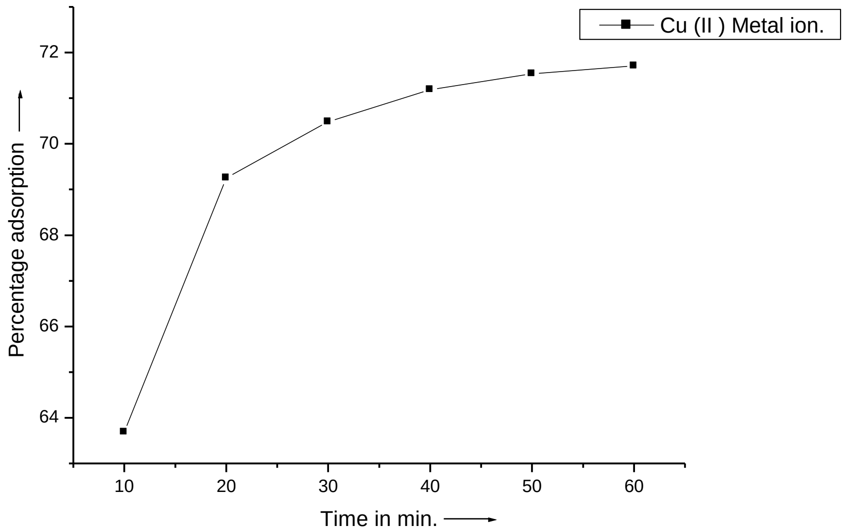

Fig.4.4.1.: Effect of contact time on percentage adsorption of Cu (II) metal ion.
[Initial conc.= 100 ppm, Adsorbent dose=1.0 g, Volume of adsorbate=100 mL, Temp=300.2 k, pH=6.1]

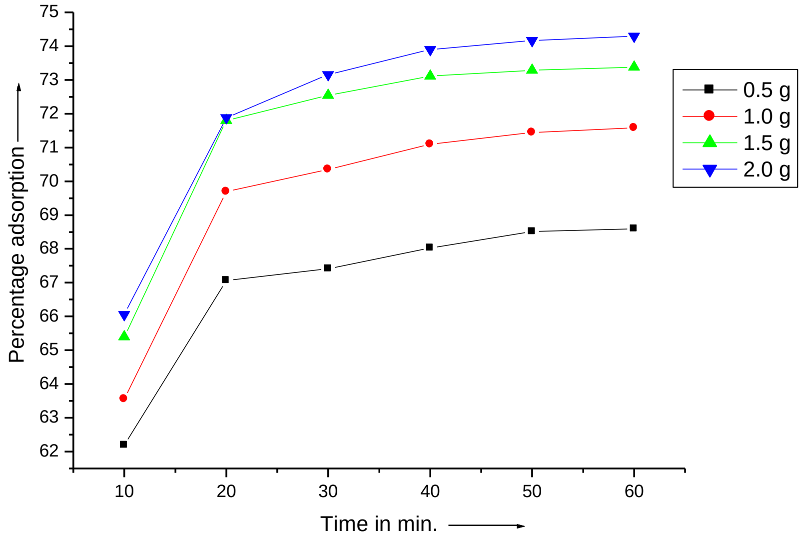

Fig.4.4.2.: Effect of adsorbent dose on percentage adsorption of Cu (II) metal ion.
[Initial conc.=100 ppm, Volume of adsorbate=100 mL, Temp=300.2 k,pH=6.1]

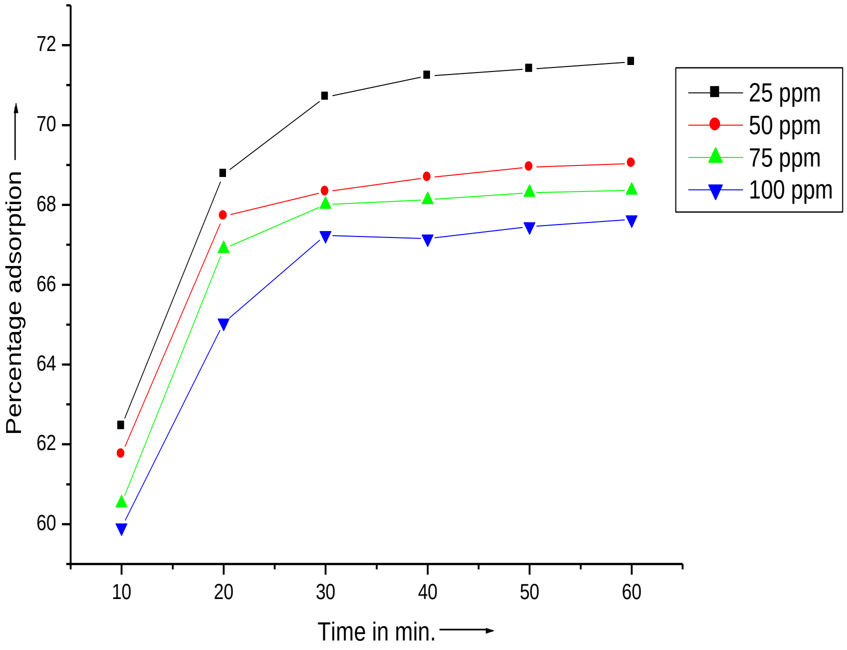

Fig.4.4.3.: Effect of initial concentration of adsorbate on percentage adsorption of Cu (II) metal ion;
[Adsorbent dose=1.0 g, Volume of adsorbate=100 mL, Temp=300.2 k, pH=6.1]

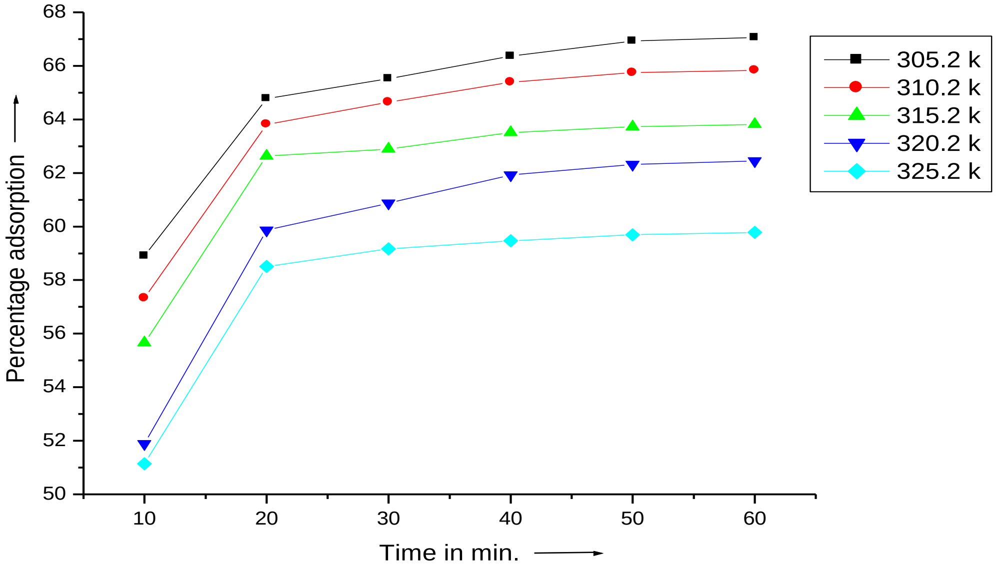

Fig.4.4.4.: Effect of temperature on percentage adsorption of Cu (II) metal ion.
[Initial conc.=100 ppm, Adsorbant dose=1.0 g, Volume of adsorbate=100 mL, pH=6.1]

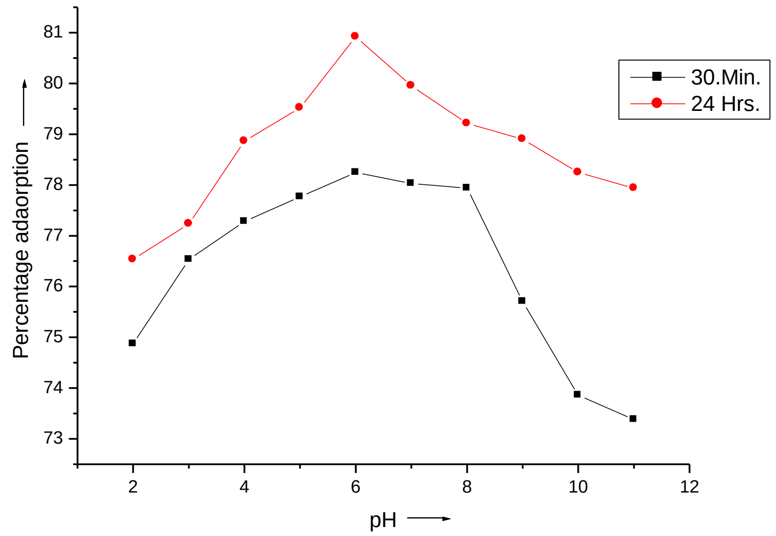

Fig.4.4.5.: Effect of pH on percentage adsorption of Cu (II) metal ion.

[Initial conc.=100 ppm, Adsorbent dose=1.0 g, Volume of adsorbate=50 mL, Temp=300.2 k]

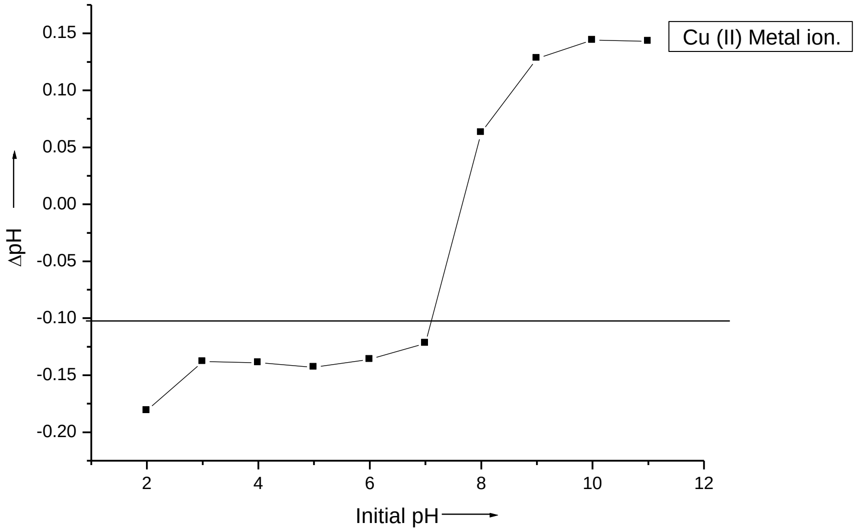

Fig.4.4.6: Effect of zero point pH on adsorption of Cu (II) metal ion.

[Initial conc.=100 ppm, Adsorbent dose=0.02 g,Volume of adsorbate=50 mL, Temp= 300.2 k]

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