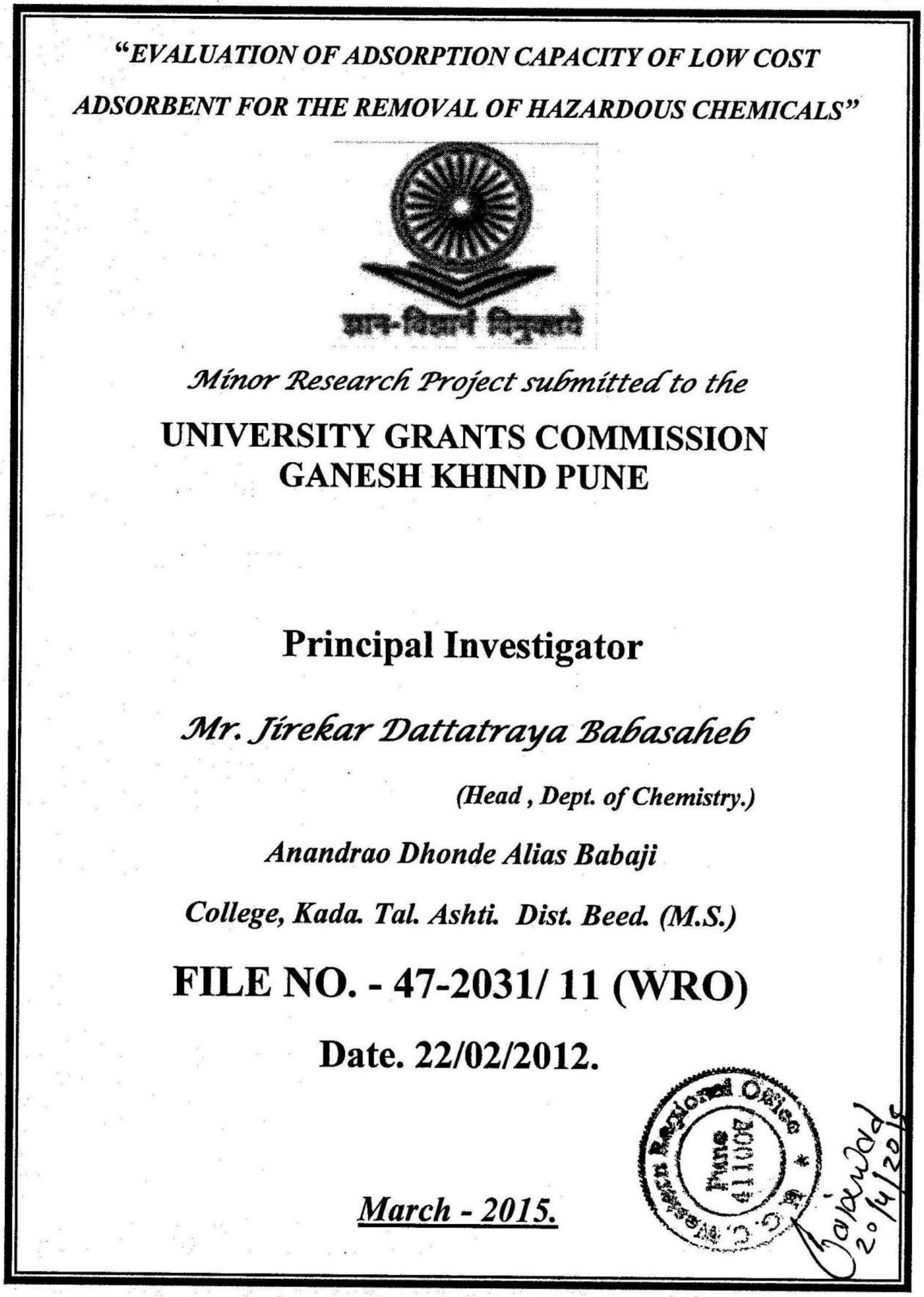

“EVALUATION OF ADSORPTION CAPACITY OF LOW COST ADSORBENT FOR THE REMOVAL OF HAZARDOUS CHEMICALS”

Minor Research Project submitted to the

UNIVERSITY GRANTS COMMISSION
GANESH KHIND PUNE

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Date : 29./07/2015.

CERTIFICATE

This is to certify that ***Mr. Jirekar Dattatraya Babasaheb*** *has satisfactory completed his minor research project in entitled"****Evaluation of adsorption capacity of low cost adsorbent for the removal of hazardous chemicals****" in the subject of Chemistry as laid down in the regulation of University Grand Commission during the academic year march-2012 to 2015.*

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Signature of the principal Investigator

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Crystal Violet	CV
Methylene Blue	MB
Chromium	Cr
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The equilibrium concentration (mg/L)	C_e
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Equilibrium rate constants	K_c
Langmuir constants relatrd to capacity of adsorption (mg/gm)	Q_0
Freundlich equation constants (adsorption intensity)	n
The amount of adsorbate adsorbed (mg/gm) at equilibrium time	q_e
The amount of adsorbate adsorbed (mg/gm) at time t	q_t
Gram	gm
Minute	min
Gibb's free energy change	ΔG^0
Enthalpy change	ΔH^0
Entropy change	ΔS^0
Concentration	Conc
Gram seed husk	GSH
Green gram seed husk	GGSH
Black gram seed husk	BGSH
Pea seed husk	PSH
Masoor seed husk	MsSH

Evaluation of Adsorption Capacity of Low Cost adsorbent For the Removal of Hazardous Chemicals

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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 pollutants 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].

In 2006 water borne diseases were estimated to cause 1- 8 million deaths each year while about 1.1 billion people lacked proper drinking water [8]. It is clear that people in the developing world need to have access to good quality water in sufficient quantity, water purification technology availability and distribution systems for water.

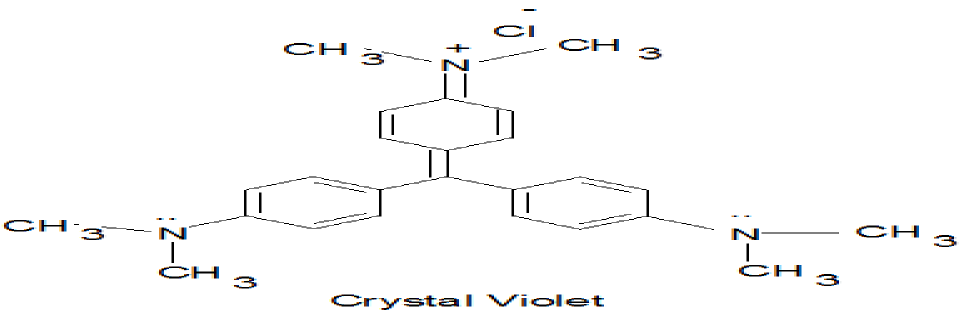
Water pollution by organic compounds has increased tremendously due to increases in industrial and animal production activity. Color stuff discharged from industries poses certain hazards and environmental problems. The colored compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into stream and affecting aquatic ecosystem. 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.

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. Due to their chemical structure dyes possess a high potential to resist fading on exposure to light and water. 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.

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 [9], activated carbon [10-12], polymers [13,14], organic molecules [15,16], pesticides [17], dyes [18,19], cosmetics [20,21], pharmaceutical paint electroplating [22,23], food tanneries, leather, dye manufacturing [24], battery manufacturing [25], metal soldering, ceramics, surface treatment, electro-galvanization [26], painting, coating, mining, extractive metallurgy, nuclear [27], and other industries. For the present study, the following dyes and metal ions were selected their properties are given in the following pages.

1.1.1 Crystal Violet (CV):

Crystal violet is a triarylmethane dye. It is widely used to dye paper and as a component of navy blue and black inks for printing, ball-point pens and ink-jet printers. It is also used to colorize diverse products such as fertilizers, anti-freezes detergents and leather jackets. It is used medically for marking the skin for surgery, finger prints, tissue-stain etc. The molecular formula is $C_{25}N_3H_{30}Cl$ and molecular weight is 407.979 gm./mole [28]. The structure of Crystal violet is shown in figure.2.



[Tris (4-(dimethylamino) phenyl) methylium chloride]

Figure: 1. Chemical structure of crystal violet.

1.1.2 Methylene Blue (MB):

It is a heterocyclic aromatic chemical compound with the 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 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. The Chemical structure of methylene blue is shown in figure 3.

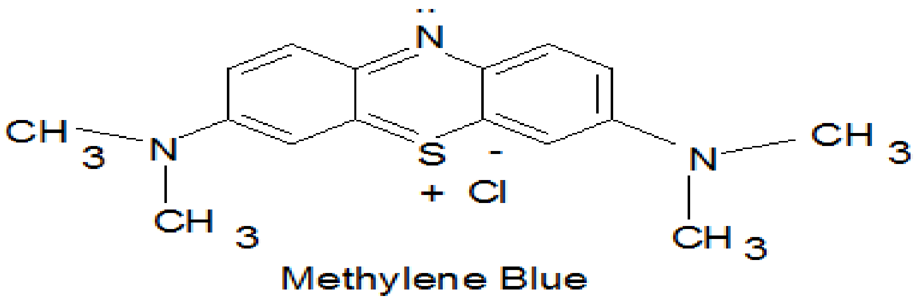


Figure: 2. Chemical structure of methylene blue

1.1.3 ***Chromium [Cr (VI)]:***

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 ***Nickel [Ni (II)]:***

Nickel is generated in the effluents from the production of stainless steel, alnico magnets, coinage, rechargeable batteries, electric guitar strings, microphone capsules, special alloys, plating, gas diffusion electrodes for alkaline fuel cells, catalysts for hydrogenation reaction and inorganic chemicals manufacturing industries are also main source of nickel pollution.

1.2 Techniques of Removal of Hazardous Materials:

The process techniques can be classified broadly into three categories physical, chemical and biological.

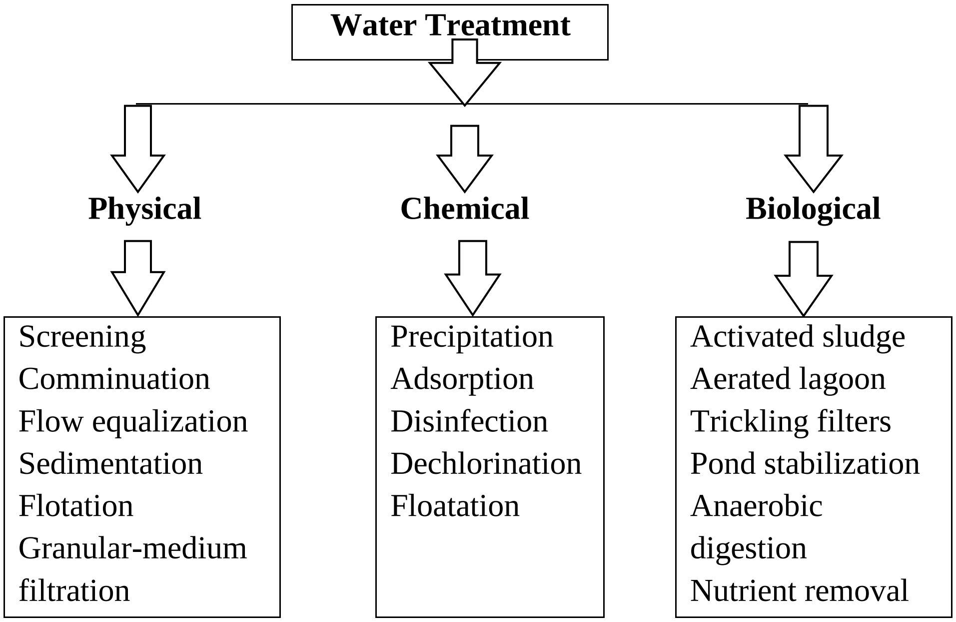


Fig.3. Classification of wastewater treatment.

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 [29], solvent extraction [30], reverse osmosis, electro-dialysis [31], precipitation [32], Biological process [33], Chemical oxidation [34], coagulation [35], ultra-filtration, phyto-extraction [36], 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 [37, 38] as well as offering the potential for regeneration, recovery and recycling of the adsorbent material. 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 [39].

Literature survey reveals that agricultural bi-products are used for the adsorption studies such as. Bale tree leaf powder [40], Leaves of Cauliflower [41], Bajara powder [42], Soya been Husk [43], Maize corn cob, jatropha oil cake, sugar cane bagasse [44], Oak wood sawdust [45], Rice straw [46], Pine Fruit [47], Almond husk [48], Banana Peel [49], Papaya seeds [50], Babul Bark [51], Coconut leaves [52], Neem leaves [53], Sawdust[54] Maize leaf [55], etc

1.3 Theories of adsorption:

1.3.1 ***Langmuir adsorption theory:*** -

Irving Langmuir was the first to derive a scientifically based adsorption isotherm in 1918 [56]. 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. 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,

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

Where, C_e (*mg/L*) is the equilibrium concentration of the adsorbate, q_e (*mg/gm*) is the amount of adsorbate adsorbed per unit mass of adsorbent, at equilibrium, Q_0 (*mg/gm*) 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 [57, 58]. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L. Which is a dimensionless constant referred to as separation factor or equilibrium parameter [59].

$$R_L = \frac{1}{1+bC_0} \qquad (2)$$

Where, C_0 is initial concentration in ppm and *b* is Langmuir constant related to the energy of adsorption. 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, $R_L = 0$.

1.3.2 ***Freundlich adsorption isotherm theory:-***

The first mathematical fit to an isotherm was published by Freundlich and Kuster in 1894, and is a purely empirical formula for gaseous adsorbates.

$$\frac{x}{m} = K_f P^{1/n} \qquad (3)$$

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 [60]. If $n = 1$ then the partition between the two phases are 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 [61]. 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 [62].

1.4 Thermodynamic Parameters:

Thermodynamic Parameters such as Gibb's free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were determined using the following equations [63-66].

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

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

Where, $$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{8}$$

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

Where, K_c is the equilibrium constant, C_{ad} is the amount of metal ion 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 [67, 68]. 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 [69, 70]. The positive value of ΔS^0 suggests that the increased disorder and randomness at the solid solution interface with adsorption.

1.5 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 [71]. The adsorption mechanism depends on the physical and chemical characteristics of adsorbent and adsorbate, pH of medium, temperature, contact time and mass transport process [72]. Various kinetic models can be suggested for an adsorption including the Lagergren pseudo-first order kinetics and pseudo-second order kinetics model [73, 74]. 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 (27) 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 experimental data is not well fitted for pseudo-first order kinetic equation as the low R^2 values. 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 (30) 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.

1.6 Selected adsorbents:-

For the present work some low-cost agricultural adsorbents were selected from dicotyledonous crop seeds are used to adsorption of heavy metal ions as well as organic dyes .These are as follows.

1.6.1 ***Gram crop:-* Gram crop (*Cicer arietinum*)** is a legume of the family Fabaceae. Its seeds are high in proteins. It grows between 20-50 cm. high and has small feathery leaves on either side of stem. It has white flowers with blue, violet or pink veins. It needs a subtropical or tropical climate with more than 400 millimeters annual rain. There are two main kinds of chickpea one is “desi” which small darker seeds and rough coat, cultivated mostly in India,. It is also known as “Kala chana”, other is Kabuli, and this has lighter coloured, larger seeds and smoother coat [75]. It is one of the earliest cultivated vegetables. Husk and bits of dal are used as nutritional feed for animals. It is a helpful source of Zinc, foliate and proteins .It has a very important role in human diet in our country.

1.6.2 ***Green gram crop:-*** Green gram crop (*Vigna radiata*) is a legume of the family Fabaceae. It is also called Mung bean. It is cultivated worldwide in tropical, semitropical and temperate climates. Mung bean is an important grain legume in several parts of Asia and is becoming increasingly used in many other countries due to its nutritional values. The Plant normally produces a large number of flowers but most of them abscise.

In India mung beans are stripped of their outer coats to make mung dal. The split bean is green with the husk and yellow when dehusked. The mung bean contains anti-oxidant and vitamin-E and $B_{1,}$ proteins, phosphorus and calcium for strong bones. As a beauty treatment its beans are used for smooth skin, stop acne, black heals, body slimming and to fertilize hair. Straw and husk are used as fodder for cattle.

1.6.3 ***Black gram crop:-*** *Vigna mungo*; known as black gram. It is a legume of the family Fabaceae. It is an erect, sub erect or trailing, densely hairy, annual herb. The tap root produces a branched root system with smooth, rounded nodules. The pods are narrow, cylindrical and up to six cm long stem 30-60 cm. long, clothed with brownish silky hairs. Leaves 3 folio late; leaflets 5–10 cm long, flowers yellow in axillary racemes, pods subcylindric; 3.8–6.3 cm long. It is extensively cultivated all over the India. Green pods of Udid are occasionally used as a vegetable. The black ripe pulse is split into dal and is most fattening food.

1.6.4 ***Pea crop:-*** Pea crop (*Pisum sativum*) is a legume of the family Fabaceae. *Pisum sativum* is an annual plant with a life cycle of one year. The pea is most commonly the small spherical seed or the seed-pod of the pod fruit *Pisum sativum*. It is a cool season crop, grown in many parts of the world planting can take place from winter to early summer depending on location. The average height of pea crop is between 18-30 inches. It is most commonly green occasionally golden yellow in color.

The pea is most commonly the small seed or the seed pod of the pod fruit *Pisum sativum*. The immature peas are used as vegetable.In India fresh peas are used in various dishes, such as matar, matar paneer, salads etc. Peas are starchy, but high in fiber, protein, vitamins, minerals, and lutein.

1.6.5 ***Masoor crop:-*** *Masoor* crop (*Lens esculent)* is a legume of the family Fabaceae. It is a 12-18 inch high, low bushy, weakly upright to semi-viny annual having the general appearance of vetch. It has many soft, hairy branches with pinnately compound leaves and numbenus oral leaflets. Flowers are white lilac pale blue the broad smooth pods are only half inch long. Each pod bears two seeds which are thin lens shaped usually smaller than pea seeds. Various color including brown and yellow.

Young pods used as vegetables. Its seeds are mostly eaten as dal; flour is used to make soups, stews, purees, and mixed with cereals to make bread and cakes.

Fig : 1. Gram (*Cicer arietinum*) crop and seeds.

Fig : 2. Green Gram (*Vigna radiata*) crop and seeds.

Fig : 3. Black Gram (*Vigna mungo*) crop and seeds.

Fig : 4. Pea (*Pisum sativum*) crop and seeds.

Fi g : 5. Masoor (*Lens culinaris*) crop and seeds.

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2. Experimental Details

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), crystal violet (CI: 4255, MW: 407.99 gm.); potassium dichromate ($K_2Cr_2O_7$), copper sulphate pentahydrate ($CuSO_4.5H_2O$) and ammonium nickel sulphate [$NiSO_4$ $(NH_4)_2.6H_2O$] supplied by Sd. Fine Chemicals Pvt. Ltd. Mumbai, diphenyl carbazide ($(C_6H_5NH.NH_2)CO$), dimethyl gloyoxime were of Reidel (India) Chemicals Pvt. Ltd., sodium diethyl dithiocarbamate, supplied by Oxford Laboratory Mumbai, citric acid, chloroform, ethylene diammine tetra acetic acid (EDTA), butyl acetate , ammonia were supplied by Qualigens Thermo Fisher Scientific India Pvt. Ltd., Mumbai. Concentrations of adsorbates like crystal violet (CV), methylene blue (MB), chromium (VI) and nickel (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).

2.1 <u>Preparation of adsorbents:</u>

The low-cost agricultural adsorbents were prepared from different dicotyledonous crop seeds such as Gram crop (*Cicer arietinum*), Green gram crop (*Vigna radiata*), Black gram crop (*Vigna mungo*), Pea crop (*Pisum sativum*) and *Masoor* crop (*Lens* esculent) was used. All the above adsorbents were used without any chemical- treatment for adsorption of heavy metal ions as well as organic dyes.

All above different dicotyledonous crops, mature and fresh seeds were purchased from local market and washed thoroughly by water before drying to remove any dust then to soak the beans overnight. The husk of soaked beans are separated from their pulses, then washed with distilled water and dried in shadow [1]. The dried husks were grinded to fine powder [2]. The homogeneous powder was obtained by passing through mesh of desired particle size (44 – 60 µm). The homogeneous fine powder adsorbent was stored in an air tight container for the adsorption study for further experiments.

2.2. <u>Preparation of adsorbates:</u>

The adsorbates selected for the present study were, the organic compounds such as Crystal Violet and Methylene Blue and the inorganic compounds (metal ions) were Chromium [Cr (VI)] and **Nickel** [Ni (II)].

2.2.1 *<u>Organic compounds:-</u>*

All the above organic compounds (Crystal Violet and Methylene Blue) are commercially available and these are purchased from different chemical laboratories such as methylene blue was purchased from Qualigens, Fine Chemicals, Mumbai (India), crystal violet was purchased from Loba Chemicals Pvt. Ltd. Mumbai (India). All solutions were prepared in double distilled water. The concentration of dye solutions were 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 [3]. The concentration of solution was determined from calibration curve spectrophotometrically at their λmax that is Crystal Violet (λmax = 540 nm) and for Methylene Blue (λmax = 570 nm).

2.2.2 Inorganic compounds (Metal ions):-

2.2.2.1 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 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 then absorbance was determined at 540 nm. Using a reagent blank as compared liquid [4].

2.2.2.2 Nickel [Ni (II)]:- Stock solution of nickel metal ion (100 ppm) was prepared by weighing and dissolving 0.675 gm. of ammonium nickel sulphate [$NiSO_4 (NH_4)_2.6H_2O$] in one liter of double distilled water in graduated volumetric flask and used to prepare different solutions. 10 ml of ammonium nickel sulphate solution was taken in a beaker containing 90 ml of water, 5.0 gm. of citric acid and finally ammonia was added to maintain the pH=7.5 Solution was transferred to a separating funnel and 20 ml dimethyl gloyoxime solution was added. After allowing the content to stand for one minute, 12 ml of chloroform was added with constant shaking. Again the solution was allowed to stand for one minute. The organic phase (red chloroform) gets separated. The absorbance was determined at 366 nm against blank was determined nickel (II) metal ion.

2.3 Parameters for Batch Adsorption Techniques:

2.3.1 Effect of contact Time:- Contact time is one of the important parameters for the assessment of practical application of adsorption process [5-8]. Adsorbent powder were 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 5, 10, 15, 20, 25, 30, 35 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 [9], and then the kinetic adsorption parameters were calculated.

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

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).*

2.3.2 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 major factors are the number of compounds in the solution, their relative adsorb abilities, initial concentration of adsorbate in the solution, and the degree of competition among solutes for adsorption sites. Different isotherm equations have been tested, namely, Langmuir, Freundlich, Temkin, etc., 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 [10].

2.3.3 *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 [11]. The percentage adsorption was calculated by following equation;

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

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

2.3.4 *Effect of Temperature:-*

*T*he adsorption experiments were performed at five different temperatures *viz*., 5,10,15,20, and 25 ^{o}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) [12-14].

2.3.5 *Effect of pH:-*

The initial pH of the solution is an important parameter, which controls the adsorption process, particularly the adsorption capacity [15]. he 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) [16] 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.

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3. Experimental Results

3.1 Adsorption study of crystal violet (CV) on low-cost materials:-

3.1.1 Effect of Contact time:-

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

Amount of adsorbent = 1.0 gm. Conc. of adsorbate = 50 ppm.

Temperature = 303.5 ± 0.3 K. pH = 6.56 Volume of adsorbate = 50 ml.

Time (min)	Absorbance and Conc. of Selected Adsorbents at different time interval.									
	GSH		*GGSH*		*BGSH*		*PSH*		*MsSH*	
	Absor bance	*Conc.*	*Absor bance*	*Conc.*	*Absor bance*	*Conc.*	*Absor bance*	*Conc.*	*Absor bance*	*Conc.*
5	1.643	14.936	1.563	14.209	1.496	13.600	1.383	12.573	1.395	12.682
10	1.591	14.464	1.507	13.700	1.439	13.082	1.268	11.527	1.261	11.464
15	1.545	14.045	1.471	13.373	1.403	12.755	1.159	10.536	1.163	10.573
20	1.508	13.709	1.446	13.145	1.372	12.473	1.061	9.6455	1.075	9.7727
25	1.479	13.445	1.429	12.991	1.351	12.282	0.995	9.0455	1.028	9.3455
30	1.457	13.245	1.417	12.882	1.333	12.118	0.938	8.5273	0.973	8.8455
35	1.449	13.173	1.409	12.809	1.324	12.036	0.884	8.0364	0.941	8.5545
24 Hrs	1.401	12.736	1.154	10.491	0.972	8.8364	0.537	4.8818	0.594	5.4000

3.1.2 Effect of Adsorbent Dose:-

Table: 3.1.2. Absorbance and Concentration of CV dye solution at different adsorbent dose.

Conc. of adsorbate = 50 ppm. Temperature = 304.9±0.3 K.

Volume of adsorbate = 50 ml. pH = 7.262 Adsorption time = 24 hrs.

Adsorbent dose (gm.)	Absorbance and Concentration of CV dye solution at different adsorbent dose.									
	GSH		***GGSH***		***BGSH***		***PSH***		***MsSH***	
	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.
0.5	1.432	13.018	1.508	13.709	1.113	10.118	1.212	11.020	1.198	10.891
1.0	0.879	7.990	1.112	10.109	0.637	5.791	0.839	7.627	0.775	7.045
1.5	0.521	4.736	0.999	9.082	0.409	3.718	0.471	4.282	0.424	3.854
2.0	0.441	4.009	0.523	4.754	0.336	3.055	0.396	3.600	0.374	3.400
2.5	0.369	3.359	0.477	4.336	0.266	2.418	0.323	2.936	0.319	2.900

3.1.3 Effect of Initial Concentration:-

Table: 3.1.3. Absorbance and Concentration of CV dye solution at different initial conc. of CV dye solution.

Amount of adsorbent = 1.0 gm. Temperature = 304.9±0.3 K.

Volume of adsorbate = 50 ml. pH = 7.262 Adsorption time = 24 hrs.

Initial conc. (ppm)	Absorbance and Concentration of CV dye solution at different initial conc.									
	GSH		***GGSH***		***BGSH***		***PSH***		***MsSH***	
	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.
25	0.824	7.491	0.568	5.164	0.478	4.345	0.268	2.436	0.431	3.918
50	1.097	9.973	0.751	6.827	0.598	5.436	0.527	4.791	0.483	4.391
75	1.337	12.154	0.947	8.609	0.858	7.800	0.570	5.182	0.624	5.673
100	1.524	13.854	1.228	11.164	0.987	8.973	0.597	5.427	0.754	6.854

3.1.4 Effect of Temperature:-

Table: 3.1.4. Absorbance and Concentration of CV dye solution at different temperature.

Amount of adsorbent = 1.0 gm. Conc. of adsorbate = 50 ppm.

Volume of adsorbate = 50 ml. pH = 6.063 Adsorption time = 24 hrs.

Temp. (K)	Absorbance and Concentration of CV dye solution at different temperature.									
	GSH		***GGSH***		***BGSH***		***PSH***		***MsSH***	
	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.
306.2	1.352	12.291	1.072	9.745	0.724	6.582	0.559	5.082	0.573	5.209
311.2	1.419	12.900	1.164	10.582	0.824	7.491	0.607	5.518	0.623	5.664
316.2	1.475	13.409	1.236	11.236	0.942	8.564	0.660	6.000	0.673	6.118
321.2	1.524	13.855	1.314	11.945	1.059	9.627	0.707	6.427	0.725	6.591
326.2	1.582	14.382	1.427	12.973	1.214	11.036	0.759	6.900	0.817	7.427

3.1.5 Effect of pH:-

Table: 3.1.5 Absorbance and Concentration of CV dye solution at different pH

Amount of adsorbent = 0.5 gm. Conc. of adsorbate = 50 ppm.

Volume of adsorbate = 25 ml. Temp. = 305.6±0.3 K. Adsorption time = 24 hrs.

Sr. No	pH	Absorbance and Concentration of CV dye solution at different pH.									
		GSH		***GGSH***		***BGSH***		***PSH***		***MsSH***	
		Absorbance	Concentration	Absorbance	Concentration	Absorbance	Concentration	Absorbance	Concentration	Absorbance	Concentration
1	2	0.393	3.573	0.267	2.427	0.470	4.273	0.206	1.870	0.273	2.482
2	3	1.154	10.491	0.255	2.318	0.267	2.427	1.348	12.255	0.208	1.891
3	4	1.517	13.791	0.993	9.027	0.913	8.300	0.671	6.100	0.524	4.764
4	5	1.536	13.964	1.229	11.173	0.766	6.964	0.649	5.900	0.567	5.154
5	6	1.532	13.927	1.175	10.682	0.821	7.464	0.635	5.773	0.651	5.918
6	7	1.528	13.891	0.989	8.991	0.632	5.745	0.672	6.109	0.632	5.745
7	8	1.531	13.918	0.812	7.382	1.067	9.700	0.754	6.854	0.957	8.700
8	9	1.539	13.991	1.038	9.436	0.985	8.954	0.762	6.927	0.792	7.200
9	10	1.523	13.845	1.214	11.036	0.968	8.800	0.957	8.700	0.734	6.673
10	11	0.695	6.3182	0.516	4.691	0.326	2.964	0.206	1.870	0.326	2.964

3.2 Adsorption study of methylene blue (MB) on low-cost materials:

3.2.1 <u>Effect of Contact time:-</u>

Table: 3.2.1. Absorbance & conc. of MB dye solution at different time interval.
Amount of adsorbent = 1.0 gm. Conc. of adsorbate = 100 ppm.
Volume of adsorbate = 50 ml. pH = 7.170 Temperature = 297.8 ± 0.3 K.

Time (min)	Absorbance and Concentrations of Selected adsorbents at different time interval.									
	GSH		*GGSH*		*BGSH*		*PSH*		*MsSH*	
	Absor bance	*Conc.*	*Absor bance*	*Conc.*	*Absor bance*	*Conc.*	*Absor bance*	*Conc.*	*Absor bance*	*Conc.*
5	1.668	34.041	1.194	24.367	1.239	25.286	0.857	17.490	1.028	20.980
10	1.607	32.796	1.092	22.286	1.153	23.531	0.793	16.184	0.832	16.980
15	1.564	31.918	1.031	21.041	1.077	21.980	0.741	15.122	0.706	14.408
20	1.541	31.449	0.984	20.082	1.019	20.796	0.719	14.673	0.663	13.531
25	1.523	31.082	0.947	19.327	0.976	19.918	0.701	14.306	0.634	12.939
30	1.511	30.837	0.933	19.041	0.953	19.449	0.687	14.020	0.617	12.592
35	1.503	30.673	0.921	18.796	0.941	19.204	0.683	13.939	0.609	12.429
24 Hrs	1.295	26.429	0.483	9.857	0.565	11.531	0.367	7.490	0.325	6.633

3.2.2 <u>Effect of Adsorbent Dose:-</u>

Table: 3.2.2. Absorbance and Concentration of MB dye solution at different adsorbent dose.
Concentration of adsorbate = 100 ppm Temperature = 299.4±0.3 K.
Volume of adsorbate = 50 ml. pH = 7.434 Adsorption time = 24 hrs.

Adsorbent dose (gm.)	Absorbance and Conc. of MB dye solution at different adsorbent dose.									
	GSH		***GGSH***		***BGSH***		***PSH***		***MsSH***	
	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.
0.5	1.361	27.776	1.075	21.939	0.962	19.633	0.919	18.750	1.104	22.531
1.0	0.706	14.408	0.561	11.449	0.501	10.224	0.478	9.755	0.521	10.630
1.5	0.465	9.490	0.369	7.531	0.334	6.816	0.315	6.429	0.339	6.918
2.0	0.353	7.204	0.275	5.612	0.247	5.041	0.233	4.755	0.256	5.224
2.5	0.279	5.694	0.217	4.429	0.196	4.000	0.186	3.796	0.203	4.143

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.

Amount of adsorbent = 1.0 gm. Temperature = 300.3±0.3 K.

Volume of adsorbate = 50 ml. pH =7.415 Adsorption time = 24 hrs.

Initial conc. (ppm)	Absorbance and Concentration of MB dye solution at different initial conc.									
	GSH		***GGSH***		***BGSH***		***PSH***		***MsSH***	
	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.
25	0.417	8.510	0.269	5.490	0.306	6.245	0.342	6.979	0.257	5.245
50	0.718	14.653	0.391	7.980	0.372	7.592	0.389	7.939	0.296	6.041
75	0.973	19.857	0.485	9.898	0.445	9.082	0.446	9.102	0.345	7.041
100	1.263	25.775	0.509	10.388	0.529	10.796	0.505	10.306	0.396	8.082

3.2.4 Effect of Temperature:-

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

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

Volume of adsorbate = 50 ml. pH =7.471 Adsorption time = 24 hrs.

Temp. (K)	Absorbance and Concentration of MB dye solution at different temperature.									
	GSH		***GGSH***		***BGSH***		***PSH***		***MsSH***	
	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	Conc.
304.8	1.026	20.939	0.597	12.184	0.628	12.816	0.856	17.469	0.504	10.286
309.8	1.148	23.429	0.715	14.592	0.704	14.367	1.005	20.510	0.552	11.265
314.8	1.249	25.490	0.831	16.959	0.762	15.551	1.184	24.163	0.599	12.224
319.8	1.335	27.245	0.993	20.265	0.826	16.857	1.357	27.694	0.643	13.122
324.8	1.423	29.041	1.083	22.102	0.897	18.306	1.436	29.306	0.691	14.102

3.2.5 Effect of pH:-

Table: 3.2.5. Absorbance and Concentration of MB dye solutionat different pH.

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

Volume of adsorbate = 25 ml. Temp. = 301.6±0.3 K. Adsorption time = 24 hrs.

Sr. No	pH	Absorbance and Concentration of MB dye solution at different pH.									
		GSH		***GGSH***		***BGSH***		***PSH***		***MsSH***	
		Absorbance	Concentration	Absorbance	Concentration	Absorbance	Concentration	Absorbance	Concentration	Absorbance	Concentration
1	2	0.394	8.041	0.377	7.694	0.613	12.510	0.465	9.490	0.239	4.877
2	3	0.662	13.510	0.572	11.673	0.556	11.347	0.382	7.796	0.115	2.347
3	4	0.795	16.224	0.684	13.959	0.709	14.469	0.409	8.347	0.282	5.755
4	5	1.208	24.653	0.729	14.878	0.715	14.592	0.394	8.041	0.336	6.857
5	6	0.972	19.837	0.735	15.000	0.691	14.102	0.401	8.184	0.347	7.082
6	7	1.284	26.204	0.824	16.816	0.573	11.694	0.325	6.633	0.356	7.265
7	8	1.438	29.347	0.862	17.592	0.508	10.367	0.368	7.510	0.412	8.408
8	9	1.427	29.122	0.918	18.735	0.524	10.694	0.637	13.000	0.349	7.122
9	10	1.535	31.326	0.983	20.061	0.642	13.102	0.682	13.918	0.445	9.082
10	11	1.683	34.347	1.227	25.041	1.065	21.735	0.656	13.388	0.641	13.082

3.3 Adsorption study of chromium [Cr (VI)] metal ion on low-cost materials:

3.3.1 Effect of Contact time:-

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

Amount of adsorbent = 0.5 gm. Conc. of adsorbate = 5 ppm.

Volume of adsorbate = 50 ml. pH = 5.489 Temperature = 301.5 ± 0.3 K

Time (min)	Absorbance and Concentrations of Selected Adsorbents at different time interval.									
	GSH		***GGSH***		***BGSH***		***PSH***		***MsSH***	
	Absor bance	*Conc.*	*Absor bance*	*Conc.*	*Absor bance*	*Conc.*	*Absor bance*	*Conc.*	*Absor bance*	*Conc.*
5	0.679	2.616	0.381	1.468	0.634	2.442	1.256	4.838	0.193	0.743
10	0.472	1.818	0.210	0.809	0.517	1.991	1.229	4.734	0.152	0.585
15	0.317	1.221	0.147	0.566	0.442	1.703	1.204	4.638	0.119	0.458
20	0.232	0.894	0.105	0.404	0.391	1.506	1.189	4.580	0.098	0.377
25	0.168	0.647	0.080	0.308	0.351	1.352	1.180	4.546	0.089	0.343
30	0.140	0.539	0.067	0.258	0.336	1.294	1.175	4.526	0.080	0.308
35	0.107	0.412	0.053	0.204	0.328	1.263	1.172	4.515	0.077	0.297
24 Hrs	0.039	0.150	0.027	0.104	0.097	0.374	0.781	3.008	0.032	0.123

3.3.2 Effect of Adsorbent Dose:-

Table: 3.3.2.(a). Absorbance and Concentrations of Chromium [Cr (VI)] metal ions at different adsorbent dose of GSH.

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

Volume of adsorbate = 50 ml pH = 7.170 Adsorption time = 24 hrs.

Adsorbent dose (gm.)	Absorbance and Conc. of Chromium metal ions at different adsorbent dose.									
	GSH		***GGSH***		***BGSH***		***PSH***		***MsSH***	
	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.
0.25	0.305	1.175	0.175	0.674	0.244	0.940	0.291	1.121	0.048	0.185
0.50	0.173	0.666	0.098	0.378	0.127	0.489	0.161	0.620	0.023	0.089
0.75	0.119	0.458	0.058	0.223	0.091	0.351	0.112	0.431	0.016	0.062
1.0	0.093	0.358	0.051	0.196	0.069	0.266	0.087	0.335	0.012	0.046

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.

Amount of adsorbent = 0.5 gm. Temperature = 301.5±0.3 K.

Volume of adsorbate = 50 ml. pH = 6.7 Adsorption time = 24 hrs.

Initial conc. (ppm)	Absorbance and Conc. of Cr (VI) metal ion solution at different initial conc.									
	GSH		***GGSH***		***BGSH***		***PSH***		***MsSH***	
	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.
5	0.143	0.551	0.139	0.535	0.209	0.805	0.823	3.170	0.146	0.562
10	0.167	0.643	0.176	0.678	0.273	1.052	0.905	3.486	0.241	0.928
15	0.212	0.817	0.213	0.820	0.325	1.252	0.937	3.609	0.305	1.175
20	0.229	0.882	0.241	0.928	0.366	1.410	0.953	3.671	0.313	1.206

3.3.4 *Effect of Temperature:-*

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

Amount of adsorbent = 0.5 gm. Conc. of adsorbate = 5 ppm.

Volume of adsorbate = 50 ml. pH = 6.5 Adsorption time = 24 hrs

Temp. (K)	Absorbance and Conc. of Chromium metal ion solution at different temperature									
	GSH		***GGSH***		***BGSH***		***PSH***		***MsSH***	
	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.
306.5	0.031	0.119	0.041	0.158	0.061	0.235	0.535	2.061	0.044	0.169
311.5	0.044	0.169	0.049	0.189	0.071	0.273	0.621	2.392	0.053	0.204
316.5	0.060	0.231	0.057	0.220	0.083	0.320	0.692	2.666	0.064	0.246
321.5	0.081	0.312	0.065	0.250	0.094	0.362	0.765	2.947	0.076	0.293
326.5	0.113	0.435	0.076	0.293	0.109	0.420	0.829	3.193	0.089	0.343

3.3.5 Effect of pH:-

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

Amount of adsorbent = 0.5 gm. Conc. of adsorbate = 5 ppm.

Volume of adsorbate = 25 ml. Temp. = 301.5±0.3 K. Adsorption time = 24 hrs.

Sr. No	pH	Absorbance and Conc. of Chromium metal ion solution at different pH									
		GSH		***GGSH***		***BGSH***		***PSH***		***MsSH***	
		Absorbance	Concentration	Absorbance	Concentration	Absorbance	Concentration	Absorbance	Concentration	Absorbance	Concentration
1	2	0.067	0.258	0.038	0.146	0.065	0.250	0.578	2.226	0.079	0.304
2	3	0.082	0.316	0.068	0.262	0.062	0.239	0.946	3.644	0.076	0.293
3	4	0.110	0.424	0.125	0.481	0.149	0.574	0.978	3.767	0.109	0.420
4	5	0.093	0.358	0.133	0.512	0.158	0.609	1.112	4.283	0.128	0.493
5	6	0.128	0.493	0.075	0.289	0.127	0.489	1.068	4.114	0.127	0.489
6	7	0.054	0.208	0.099	0.381	0.099	0.381	1.187	4.572	0.069	0.266
7	8	0.074	0.285	0.140	0.539	0.109	0.420	1.144	4.407	0.109	0.420
8	9	0.076	0.293	0.101	0.389	0.091	0.350	1.049	4.041	0.091	0.350
9	10	0.075	0.289	0.103	0.397	0.117	0.451	1.107	4.264	0.117	0.451
10	11	0.081	0.312	0.143	0.551	0.144	0.555	0.889	3.424	0.144	0.555

3.4 Adsorption study of nickel [Ni (II)] metal ion on low-cost materials:-

3.4.1 Effect of Contact time:-

Table: 3.4.1. Absorbance & conc. of Nickel [Ni (II)] metal ions at different time interval.

Amount of adsorbent = 0.5 gm. Conc. of adsorbate = 20 ppm.

Volume of adsorbate = 50 ml. pH = 5.889 Temperature = 303.0 ± 0.3 K.

Time (min)	Absorbance and Concentrations of Selected Adsorbents at different time interval.									
	GSH		**GGSH**		**BGSH**		**PSH**		**MsSH**	
	Absor bance	*Conc.*	*Absor bance*	*Conc.*	*Absor bance*	*Conc.*	*Absor bance*	*Conc.*	*Absor bance*	*Conc.*
5	1.002	5.475	0.997	5.448	1.001	5.470	0.995	5.437	0.988	5.399
10	0.963	5.262	0.962	5.257	0.953	5.208	0.947	5.175	0.931	5.087
15	0.931	5.087	0.934	5.104	0.921	5.033	0.908	4.962	0.894	4.885
20	0.909	4.967	0.911	4.978	0.894	4.885	0.871	4.760	0.869	4.749
25	0.891	4.869	0.893	4.880	0.872	4.765	0.840	4.590	0.853	4.661
30	0.875	4.781	0.876	4.787	0.859	4.694	0.819	4.475	0.842	4.601
35	0.868	4.743	0.867	4.738	0.851	4.650	0.811	4.432	0.837	4.574
24 Hrs	0.810	4.426	0.809	4.421	0.812	4.437	0.720	3.934	0.727	3.973

3.4.2 Effect of Adsorbent Dose:-

Table: 3.4.2. Absorbance and Conc. of Nickel [Ni (II)] metal ion at different adsorbent dose of GSH.

Conc. of adsorbate = 20 ppm Temperature = 303.5±0.3 K

Volume of adsorbate = 50 ml pH = 5.7 Adsorption time = 24 hrs.

Adsorbent dose (gm.)	Absorbance and Conc. of Nickel metal ion at different adsorbent dose.									
	GSH		**GGSH**		**BGSH**		**PSH**		**MsSH**	
	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.
0.25	0.793	4.333	0.854	4.667	0.795	4.344	0.762	4.164	0.827	4.520
0.50	0.414	2.262	0.421	2.300	0.412	2.251	0.394	2.153	0.375	2.049
0.75	0.271	1.481	0.275	1.503	0.263	1.437	0.257	1.404	0.241	1.317
1.0	0.202	1.104	0.207	1.131	0.198	1.082	0.191	1.044	0.176	0.962

3.4.3 Effect of Initial Concentration:-

Table: 3.4.3. Absorbance and Conc. of Nickel [Ni (II)] metal ions at different initial Conc. of solution.

Amount of adsorbent = 0.5 gm. Temperature = 304.5±0.3 K.

Volume of adsorbate = 50 ml. pH = 5.7 Adsorption time = 24 hrs.

Initial conc. (ppm)	Absorbance and Conc. of Nickel metal ion solution at different initial conc.									
	GSH		**GGSH**		**BGSH**		**PSH**		**MsSH**	
	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.	Absor bance	Conc.
5	0.276	1.508	0.504	2.754	0.537	2.934	0.539	2.945	0.436	2.382
10	0.358	1.956	0.567	3.098	0.592	3.235	0.607	3.317	0.464	2.535
15	0.510	2.787	0.675	3.688	0.723	3.951	0.669	3.656	0.652	3.563
20	0.584	3.191	0.801	4.377	0.738	4.033	0.735	4.016	0.739	4.038

3.4.4 Effect of Temperature:-

Table: 3.3.4. Absorbance and Conc. of Nickel [Ni (II)] metal ions at different temperature of solution.

Amount of adsorbent = 0.5 gm. Conc. of adsorbate = 20 ppm.

Volume of adsorbate = 50 ml. pH = 5.7 Adsorption time = 24 hrs.

Temp. (K)	Absorbance and Concentration of Nickel metal ion solution at different temperature									
	GSH		**GGSH**		**BGSH**		**PSH**		**MsSH**	
	Absor bance	Conc	Absor bance	Conc	Absor bance	Conc	Absor bance	Conc	Absor bance	Conc
306.5	0.649	3.546	0.864	4.721	0.874	4.776	0.722	3.945	0.654	3.574
311.5	0.691	3.776	0.876	4.787	0.884	4.831	0.757	4.137	0.682	3.727
316.5	0.729	3.984	0.890	4.863	0.895	4.891	0.792	4.328	0.714	3.902
321.5	0.765	4.180	0.903	4.934	0.905	4.945	0.829	4.530	0.746	4.077
326.5	0.804	4.393	0.917	5.011	0.916	5.005	0.864	4.721	0.779	4.257

3.4.5 *Effect of pH:-*

Table: 3.4.5. Absorbance and Conc. of Nickel [Ni (II)] metal ions at different pH of solution.

Amount of adsorbent = 0.5 gm. Conc. of adsorbate = 20 ppm.

Volume of adsorbate = 25 ml. Temp. = 303.0±0.3K. Adsorption time = 24 hrs.

Sr. No	pH	Absorbance and Concentration of Nickel [Ni (II)] metal ion solution at different pH.									
		GSH		***GGSH***		***BGSH***		***PSH***		***MsSH***	
		Absorbance	Concentration	Absorbance	Concentration	Absorbance	Concentration	Absorbance	Concentration	Absorbance	Concentration
1	2	1.041	5.688	1.038	5.672	1.037	5.667	1.038	5.672	1.036	5.661
2	3	0.871	4.760	1.027	5.612	1.001	5.470	0.892	4.874	0.887	4.847
3	4	0.679	3.710	1.008	5.508	0.905	4.945	0.634	3.464	0.833	4.552
4	5	0.740	4.044	1.021	5.579	0.539	2.945	0.713	3.896	0.735	4.016
5	6	0.748	4.087	1.015	5.546	0.865	4.727	0.717	3.918	0.758	4.142
6	7	0.830	4.535	1.025	5.601	0.984	5.377	0.905	4.945	0.829	4.530
7	8	0.382	2.087	1.005	5.492	0.928	5.071	0.735	4.016	0.750	4.098
8	9	1.021	5.579	0.773	4.224	0.927	5.066	0.812	4.437	0.758	4.142
9	10	0.707	3.863	0.970	5.300	0.926	5.060	0.908	4.962	0.996	5.443
10	11	0.412	2.251	0.807	4.410	1.029	5.623	0.466	2.546	0.796	4.350

4. Result and Discussion

4.1 Adsorption study of crystal violet (CV) on low-cost materials:-

4.1.1 ***<u>Effect of contact time:-</u>*** The agricultural materials such as GSH, GGSH, BGSH, PSH, and MsSH, have been used as a adsorbents for the removal of CV from its aqueous solutions.

The effect of contact time on the amount of CV adsorbed was investigated at various time intervals and the remaining parameters were kept constant, samples were taken and the absorbance was measured. The percentage adsorption of CV increased with increase with in contact time, the results were presented in Fig. 4.1.1. The observed trend of percentage adsorption of CV with adsorbents was PSH>MsSH>BGSH>GGSH >GSH.

4.1.2 ***<u>Effect of adsorbent dose:-</u>*** The effect of amount of the adsorbents was *necessary in order to observe the minimum possible amount, which s*hows maximum adsorption. It was studied by using different amount of dose like 0.50, 1.0, 1.5, 2.0, 2.5 gm. for the initial concentration that is 50 mg/L.at 304.9±0.3K, pH 7.262 and contact time 24 hours. The percentage adsorption of CV increased with increase with in the amount of adsorbents (Fig.4.1.2.). The observed trend of percentage adsorption of CV with adsorbents was PSH>MsSH>BGSH>GGSH>GGSH.

4.1.3 ***<u>Effect of initial concentration:-</u>***The adsorption experiments were performed in the concentration range (25-100mg/L) at pH 7.20, adsorbent dose 1.0gm and temperature 304.9±0.3K (Table 3.2.3.(a)-3.2.3.(i)), the initial CV concentration was plotted against percentage adsorption of CV (Fig.4.1.3.). The percentage adsorption of CV increases with increase initial concentration [1]. The observed trend shows that with adsorbents PSH>MsSH>BGSH>GGSH>GSH. Similar observations were noted from the previous workers [2-4].

4.1.4 ***<u>Effect of temperature:-</u>*** The effect of adsorption rate was carried out at different temperatures, with rising temperature from 306.2, 311.2, 316.2, 321.2, and 326.2 K within 24 hours for 50 mg/L, it was observed that percentage adsorption of CV decreases with increase in temperature (Fig.4.1.4.) the observed trend shows that with adsorbents PSH>MsSH>BGSH>GGSH>GSH.

4.1.5 ***<u>Effect of pH:-</u>*** The PH can influence the adsorption of CV; the experiments were carried out at different PH (Table 4.1.2.). The observed trend shows that MsSH>BGSH>PSH>GSH>GGSH, (Fig.4.1.5.). These were in accordance with previous researches [5]. It was clear that the adsorption process was highly dependent on the pH of the solution, the higher percentage adsorption in acidic range as well as basic range was due to the fact that surface becomes negatively charged, thus making $[H^+]$ ions complete effectively with CV cations causing increases in the adsorption .

4.1.6 ***Adsorption kinetics:-***The values of R^2 with first order were in the range of 0.998 to 0.936. While for second order R^2 values were in the range of 1.00 to 0.999 adsorbents.

Table: 4.1.1. Kinetic parameter values with CV:-

Amount of adsorbent = 1.0 gm. Conc. of adsorbate = 50 ppm.
Volume of adsorbate = 50 ml. pH = 6.566 Temperature = 303.5 ± 0.3 K.

Adsorbents	***Pseudo-first order***			***Pseudo-second order***		
	K_1 (min^{-1})	***q_e (mg/gm.)***	***R^2***	***K_2 (gm./mg.min)***	***q_e (mg/gm.)***	***R^2***
GSH	$56.516*10^{-3}$	148.888	0.995	$1.215*10^{-3}$	1861.840	0.999
GGSH	$15.338*10^{-3}$	188.530	0.938	$1.762*10^{-3}$	1873.842	0.999
BGSH	$13.127*10^{-3}$	243.759	0.959	$1.476*10^{-3}$	1914.700	0.999
PSH	$29.870*10^{-3}$	443.374	0.998	$0.425*10^{-3}$	2148.154	0.999
MsSH	$27.935*10^{-3}$	401.134	0.987	$5.048*10^{-3}$	2118.056	0.999

The observed trend shows that first order kinetics with adsorbents PSH>GSH>MsSH>BGSH>GGSH. While for second order, BGSH=GGSH=PSH=GSH =MsSH, the results were presented in Table. 4.1.1. It was confirmed that the adsorption kinetics was pseudo second order. This observation is in agreement with many other studies of kinetics of adsorption of CV dyes [6-9]**.**

4.1.7 ***Adsorption isotherm:-*** Langmuir and Freundlich isotherm models were often used to describe equilibrium adsorption isotherm. The Langmuir isotherm constants, adsorption equilibrium *(b) (L/mg)*, and the saturated monolayer adsorption capacity (Q_0) *(mg/g)*, were calculated from the slope and intercept (plotting the graph between *Ce/Qe and Ce)* [10]. Based on the above analysis of the adsorption, the separation factor *(R_L)* was calculated. There were four probabilities for the value of R_L (i) for unfavorable adsorption if $R_L > 1$, (ii) for linear adsorption $R_L = 1$, (iii) for favorable adsorption $0 < R_L < 1$ and (iv) for irreversible adsorption $R_L = 0$ [11]. R_LValues were for the range of 0.998 to 0.999. (Table 4.1.2.).

Table: 4.1.2. Isotherm parameter values with CV:-

Conc. of adsorbate = 50 ppm. Volume of adsorbate = 50 ml.
Temperature = 304.9±0.3 K. pH = 7.262 Time = 24 hours.

Adsorbents	***Langmuir constants***				***Freundlich constants***		
	Q_0 (mg/gm.)	***$b *10^{-6}$ (L/gm.)***	***R_L***	***R^2***	***n***	***K_f $(mg/gm.(L/gm))^{1/n}$***	***R^2***
GSH	434.783	8.119	0.999	0.980	1.033	6.045	0.984
GGSH	909.091	5.349	0.999	0.862	1.001	4.175	0.843
BGSH	833.333	3.062	0.999	0.997	1.006	7.936	0.997
PSH	588.235	5.281	0.999	0.977	1.002	6.522	0.968
MsSH	87.719	34.918	0.998	0.955	1.001	6.931	0.965

Since R_L values lies between 0 to 1 for CV adsorption studies indicates that the adsorption of CV is favorable. The data reveal that the Langmuir model yields better fit than the Freundlich model. The observed trend shows that the GSH=BGSH=PSH=GGSH>MsSH. It is clearly indicating the favorability of the adsorption process for all adsorbents. Freundlich adsorption isotherm is one of the most widely used empirical equation, which was fitted with the experimental data, the Freundlich isotherm constants were the adsorption capacity *(K_f)* and adsorption intensity (n), The n values were for adsorbents from 1.000 to 1.033. The observed trend shows that with adsorbents GSH>BGSH>PSH>GGSH=MsSH. (Table 4.1.2.). These agree with previous workers, the exponent 1/n was usually less than 1.0 because sites with the highest binding energies were utilized first, followed by weaker sites, and so on [12], the mathematical calculations of n values between 1 and 10 represent the best adsorption[13]

4.1.8 ***<u>Thermodynamics of adsorption:-</u>*** 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 4.1.3. and Table 4.1.4.).

Table: 4.1.3. Free energy change ($\Delta G°$) of CV solution at different temperature:-

Conc. of adsorbate = 50 ppm. Volume of adsorbate = 50 ml.
Amount of adsorbent = 1.0 gm. pH = 6.063 Time = 24 hours.

Temp (K)	Free energy change (ΔG°) of CV solution at different adsorbent with different temperature in KJ/mole.				
	GSH	*GGSH*	*BGSH*	*PSH*	*MsSH*
306.2	-2.842	-3.610	-4.800	-5.602	-5.198
311.2	-2.746	-3.426	-4.463	-5.458	-5.016
316.2	-2.650	-3.242	-4.127	-5.314	-4.835
321.2	-2.553	-3.058	-3.790	-5.170	-4.653
326.2	-2.457	-2.874	-3.454	-5.026	-4.472

The negative values of ΔG^0 indicates that the adsorption of CV on all adsorbent were thermodynamically feasible and spontaneous at room temperature. The ΔG^0 values obtained were in the physical adsorption (Table 4.1.3). It has been reported that ΔG^0 up to -20 KJ/mole are consistent with electrostatic interaction between sorption sites and the CV dye (physical adsorption), while ΔG^0 values more negative than -40 KJ/mole involve charge sharing or transfer from the adsorbent surface to the CV dye to form a co-ordinate bond (chemical adsorption). The ΔG^0 values obtained for CV studies are < -10 KJ/mole. which indicate that physical adsorption was the predominant mechanism in the adsorption process. The values of ΔH^0 were adsorbent in the range of –25.411 to – 4.623. In this present study, ΔH^0 was found to be less than - 40 KJ/mole. The observed trend shows that with adsorbents BGSH>MsSH>GGSH>PSH>GSH. The negative values of ΔH^0 confirmed that the adsorption was exothermic in nature, it also explained that energy was liberated by the system during adsorption process, while the negative ΔS^0 values were suggested that there was no significant changes occurred in the internal structure of the adsorbent (Table 4.2.5). Moreover, the values of ΔH^0 were less than 40 KJ/ mole, which indicated the physical adsorption [14, 15]. All these indicating that the process is slightly exothermic in nature. This is probably due to tendency of CV molecules to escape from the solid phase to bulk phase with an increase in temperature of the solution, the same trend is observed for all adsorbents [16]

Table: 4.1.4. Thermodynamic parameter values with CV solution:-

Conc. of adsorbate = 50 ppm. Volume of adsorbate = 50 ml.

Amount of adsorbent = 1.0 gm. pH = 6.063 Time = 24 hours.

Thermod-ynamic parameters	$\Delta H°$ and $\Delta S°$ values of CV solution at different adsorbent.				
	GSH	*GGSH*	*BGSH*	*PSH*	*MsSH*
$-\Delta H°$ KJ/mole	8.740	14.871	25.411	14.417	16.318
$-\Delta S°$ J/mole	19.262	36.778	67.313	28.788	35.314

4.1.9 ***<u>Conclusion:-</u>*** Based on results, percentage adsorption on different adsorbents such as GSH, GGSH, BGSH, PSH, and MsSH, were effective for percentage adsorption of CV from aqueous solutions, the operational parameters such as contact time, adsorbent dose, initial concentration, temperature, pH, etc. were studied. The percentage adsorption capacity of CV increased with increasing adsorbent dosage, contact time, initial concentration of CV solution while decreased with increasing temperature, initial pH of CV solution. The CV adsorption equilibrium was attained after 24 hours.

The kinetics of adsorption of CV was studied by using pseudo first and pseudo second order kinetic equations for the experimental data; pseudo second order kinetic model provided the best correlation of the experimental data. The kinetics of CV the adsorption fit well with the pseudo second order rate model, so the kinetic studies showed that the adsorption followed by pseudo second order rate kinetic model. The R_L values have been calculated using Langmuir constants, the values were $0 < R_L < 1$ showed that the adsorbents were favorable for the adsorption of CV. The n values between 1 and 10 represent the best adsorption. The negative value of ΔH^0 and ΔS^0 showed the adsorption is spontaneous and exothermic nature. The main results of investigation showed that all adsorbents have considerable potential for the adsorption of CV from aqueous solution. The main advantages, these low cost materials are available freely, locally, abundantly and easy to prepare in large scale and have been proven to be much more efficient than the conventional expensive adsorbents. Therefore a conclusion can be drawn that all adsorbents can be successfully used for the adsorption of CV from aqueous solution.

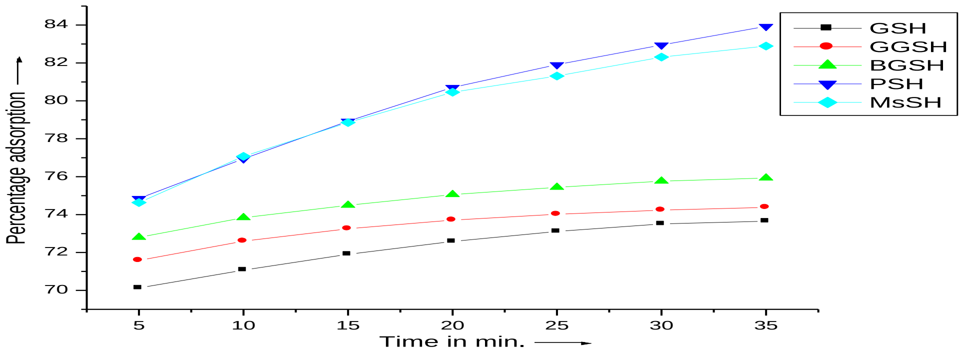

Fig 4.1.1. Effect of contact time on adsorption of CV with adsorbents.

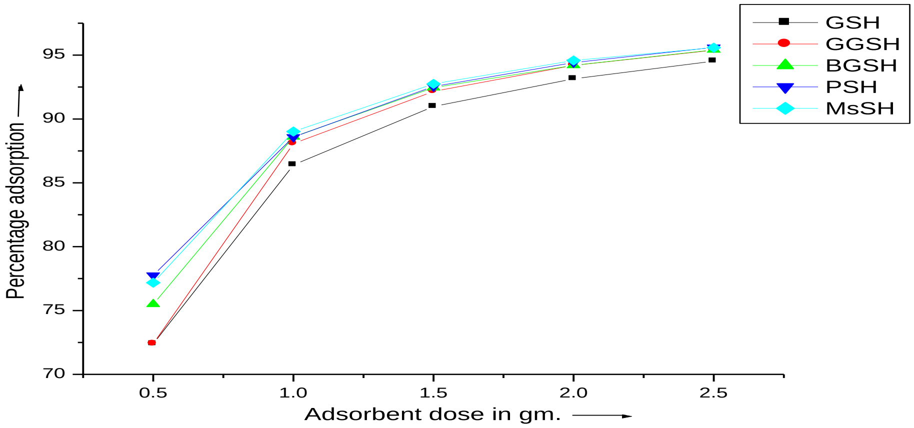

Fig 4.1.2. Effect of adsorbent dose on adsorption of CV with adsorbents.

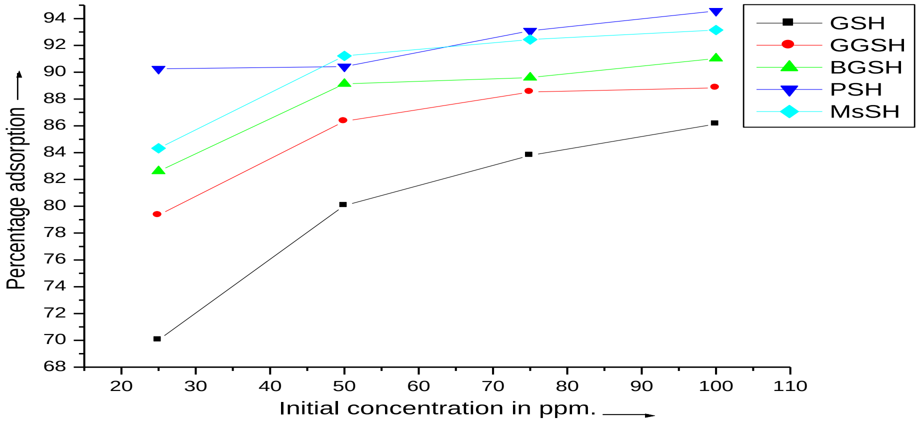

Fig 4.1.3. Effect of initial concentration on adsorption of CV with adsorbents.

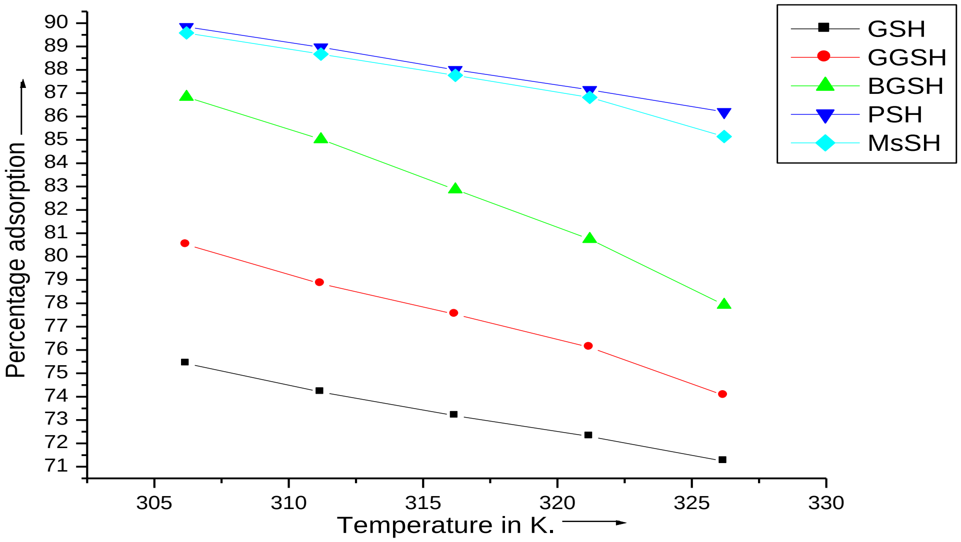

Fig 4.3.4. Effect of temperature on adsorption of CV with adsorbents.

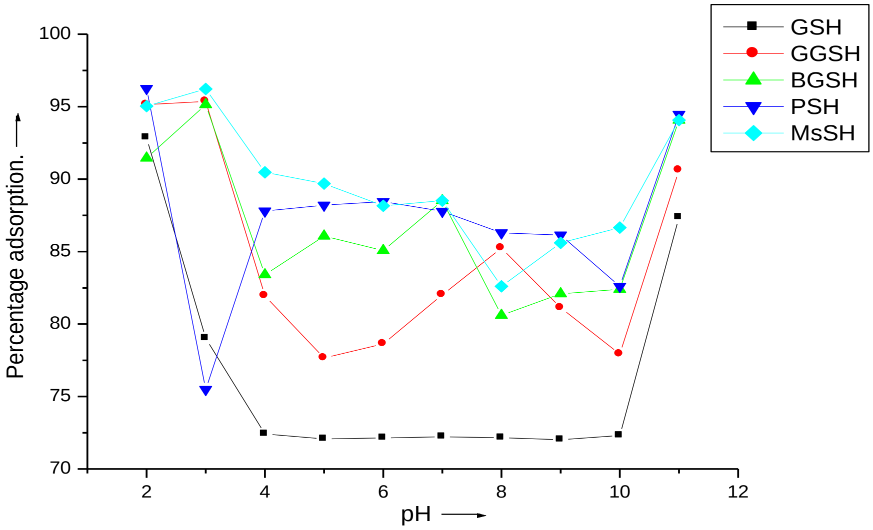

Fig 4.1.5. Effect of pH on adsorption of CV with adsorbents.

4.2 Adsorption study of methylene blue (MB) on low-cost materials:-

4.2.1 ***Effect of contact time:-*** The agricultural materials such as GSH, GGSH, BGSH, PSH, and MsSH have been used as a adsorbents for the removal of MB from its aqueous solutions. All solutions were prepared in double distilled water. For each experiment, 50 ml of MB dye solution was continuously stirred with 1.0 gm. 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 4.2.1.), the percentage adsorption of MB increasing with increasing in time and becomes constant after 35 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. The observed trends shows that with adsorbents MsSH>PSH>GGSH>BGSH>GSH.

4.2.2 ***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 gm. in each case. From the observation results, the optimum dose of adsorbent fixed for all adsorbents is 1.0 gm. It can also be seen from Fig.4.2.2, which after dosage of 1.0 gm. 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 [17]. The decreasing order of percentage adsorption of MB is PSH>BGSH>MsSH>GGSH> GSH. Similar results have been reported in literature [18].

4.2.3 ***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. GSH, GGSH, BGSH, PSH, MsSH, 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 increase initial concentration [19]. The observed trend shows that with adsorbents MsSH>BGSH>PSH>GGSH>GSH (Fig.4.2.3). Similar observations were noted from the previous workers.

4.2.4 <u>Effect of temperature:-</u> Temperature has important effect on adsorption was investigated in the temperature range of 304.2, 309.2, 314.2, 319.2, 324.2 K and 100 mg/L. 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 n 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 [20, 21].

4.2.5 <u>Effect of pH:-</u> pH is an important factor in controlling the adsorption of MB dye onto adsorbent. The adsorption of MB ions on GSH, GGSH, BGSH, PSH, and MsSH was studied at a temperature of 301.6±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 result indicates that all the selected adsorbents showed good adsorption capacity in acidic medium than in basic medium. The percentage adsorption of MB dye of adsorption on all adsorbents 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 ions 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 ions. However, a favorable increase in percentage adsorption for all adsorbents was observed below pH 7.0. The observed trend shows that with all adsorbents the maximum percentage adsorption of MB was of MsSH> PSH>GGSH>
BGSH>GSH (Fig. 4.2.6.).

4.2.6 <u>Adsorption kinetics:-</u> 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 q_e for all adsorbents are in Table 4.2.1.

Table: 4.2.1. Kinetic parameter values with MB:-

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

Volume of adsorbate = 50 ml. pH = 7.170 Temperature = 297.8 ± 0.3 K.

Adsorbents	***Pseudo-first order***			***Pseudo-second order***		
	K_1 (min^{-1})	q_e (mg/gm.)	R^2	K_2 (gm./mg.min)	q_e (mg/gm)	R^2
GSH	18.954*10^{-3}	386.563	0.934	0.741*10^{-3}	3500.885	0.999
GGSH	15.891*10^{-3}	734.988	0.931	0.428*10^{-3}	4121.553	0.999
BGSH	20.001*10^{-3}	724.569	0.959	0.355*10^{-3}	4112.671	0.999
PSH	14.302*10^{-3}	500.887	0.906	0.718*10^{-3}	4341.088	0.999
MsSH	33.440*10^{-3}	677.797	0.856	0.326*10^{-3}	4468.195	0.999

The values of (R^2) with first order were in the range of 0.984 to 0.856. The observed trend shows that with adsorbents for first order kinetics BGSH>GSH>GGSH>PSH>MsSH, while for second order (R^2) value was 0.999 for all adsorbents. The values of (R^2) obtained from pseudo second-order model were higher than pseudo first-order model, indicating that the adsorption process followed the pseudo second-order model for entire adsorption period [22, 23].

4.2.7 ***Adsorption isotherm:-*** In this study, adsorption isotherms data was correlated using two well-known adsorption equations, Langmuir and Freundlich models [24].

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. The R_L values were equal for all adsorbents (0.999). The *n* values were for adsorbents from 1.236 to 1.112 (Table 4.2.2.). The observed trend shows that with adsorbents MsSH>GSH>GGSH>PSH>BGSH. 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, $R_L = 0$ [25-30]. 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. The values of n suggests that deviation from linearity, if n = 1 the adsorption is homogenous and there is no interaction between adsorbed species. The values of n greater than unity, ($1 < n < 10$), that means favorable adsorption.[31]. The values of *n* has calculated and presented in Table:4.2.2. The values were found to be between 1 and 10, this indicates favorable adsorption.

Table: 4.2.2. Isotherm parameter values with MB:-
Conc. of adsorbate = 100 ppm. Volume of adsorbate = 50 ml.
Temperature = 299.4±0.3 K. pH = 7.434

Adsorbents	***Langmuir constants***				***Freundlich constants***		
	Q_0 (mg/gm.)	***b *10^{-6} (L/gm.)***	***R_L***	***R^2***	***n***	***K_f (mg/gm.(L/gm))$^{1/n}$***	***R^2***
GSH	857.545	3.276	0.999	0.999	1.180	8.7676	0.999
GGSH	868.598	4.858	0.999	0.999	1.138	10.3836	0.999
BGSH	707.709	6.572	0.999	0.999	1.112	11.0599	0.999
PSH	968.364	5.163	0.999	0.999	1.113	11.6761	0.999
MsSH	674.878	6.892	0.999	0.999	1.213	12.2369	0.996

4.2.8 <u>Thermodynamics of adsorption:-</u> 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 4.2.3.), the values of ΔH^0 were adsorbent in the range of -31.554 to - 9.453. The observed trend shows that with adsorbents PSH>GGSH>GSH>BGSH>MsSH. The negative values of ΔG^0 indicates that the adsorption of MB on all adsorbent were thermodynamically favorable and spontaneous nature of adsorption and confirmed affinity of natural adsorbents for MB basic dye. The ΔG^0value decreases with increase in temperature, it in Table 4.2.3.

Table: 4.2.3. Free energy change *($\Delta G°$)* of MB solution at different temperature:-
Conc. of adsorbate = 100 ppm. Volume of adsorbate = 50 ml.
Amount of adsorbent = 1.0 gm. pH = 7.471 Time = 24 hours.

Temp (K)	Free energy change (ΔG°) of MB solution at different adsorbent with different temperature in KJ/mole				
	GSH	*GGSH*	*BGSH*	*PSH*	*MsSH*
304.8	-3.322	-4.977	-4.834	-3.929	-5.477
309.8	-3.086	-4.565	-4.634	-3.475	-5.326
314.8	-2.850	-4.152	-4.434	-3.022	-5.175
319.8	-2.615	-3.740	-4.234	-2.569	-5.023
324.8	-2.379	-3.327	-4.035	-2.116	-4.872

It has been reported that ΔG^0 up to -20 KJ/mole are consistent with electrostatic interaction between sorption sites and the dye (physical adsorption), while ΔG^0 values more negative than -40 KJ/mole involve charge sharing or transfer from the adsorbent surface to the dye to form a co-ordinate bond (chemical adsorption). The ΔG^0 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.

Table: 4.2.4. Thermodynamic parameter values with MB solution:-

Conc. of adsorbate = 100 ppm. Volume of adsorbate = 50 ml.
Amount of adsorbent = 1.0 gm. pH = 7.471 Time = 24 hours.

Thermod-ynamic parameters	ΔH° and ΔS° values of MB at different adsorbent.				
	GSH	*GGSH*	*BGSH*	*PSH*	*MsSH*
$-\Delta H^\circ$ KJ/mole	17.689	30.132	17.011	31.554	14.693
$-\Delta S^\circ$ J/mole	47.137	82.527	39.953	90.633	30.236

The negative values of ΔH^0 confirmed that the adsorption was exothermic in nature, it also explained that energy was liberated by the system during adsorption process, while the negative ΔS^0 values were suggested that there was no significant changes occurred in the internal structure of the adsorbent. Moreover, the values of ΔH^0 were less than 40 KJ/ mole, which indicated the physical adsorption [32, 33]. 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, the same trend is observed for all adsorbents [34].

4.2.9 ***Conclusion:-***The adsorption of MB from aqueous solution using adsorbents viz. GSH, GGSH, BGSH, PSH, and MsSH powders was investigated. Different important factors like contact time, adsorbent dose, initial concentration of MB, temperature and initial pH of solution were optimized. The adsorption experiments shows that all the above low-cost adsorbents were 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 achives 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 and initial concentration of MB dye solution used, while the percentage adsorption decreased with the increase in temperature. Equilibrium data very well fitted in a Langmuir and Freundlich isotherm models, confirming the adsorption capacity of MB onto adsorbents (GSH, GGSH, BGSH, PSH, and MsSH) 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^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) studies indicates that, the negative values of ΔG^0 indicated the spontaneous nature of adsorption, physical adsorption and confirmed affinity of adsorbents for the MB basic dye. Negative value of ΔH^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 all adsorbents are 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.

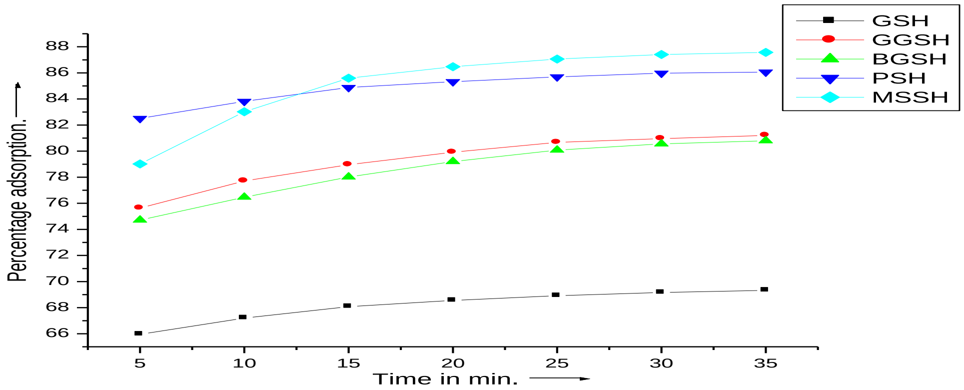

Fig:4.2.1. Effect of contact time on adsorption of MB with adsorbents.

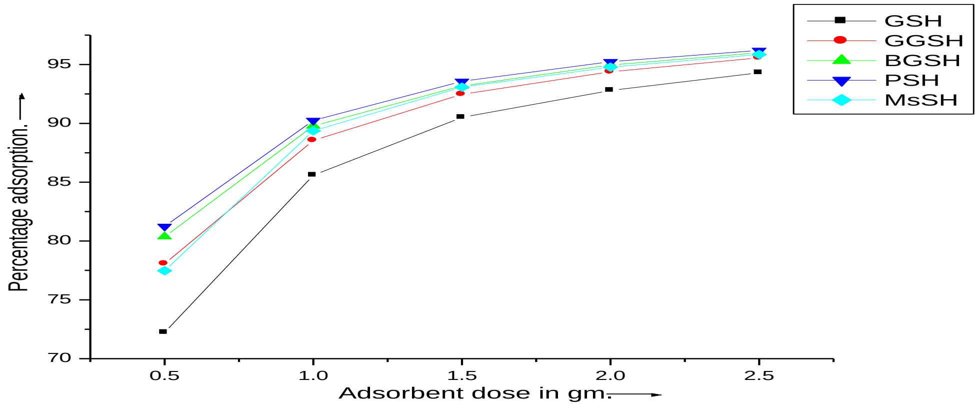

Fig:4.2.2. Effect of adsorbent dose on adsorption of MB with adsorbents.

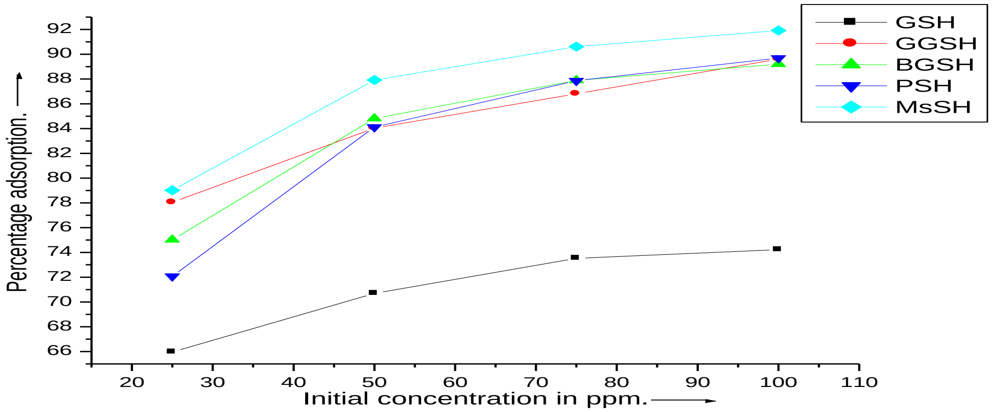

Fig:4.2.3. Effect of initial concentration on adsorption of MB with adsorbents.

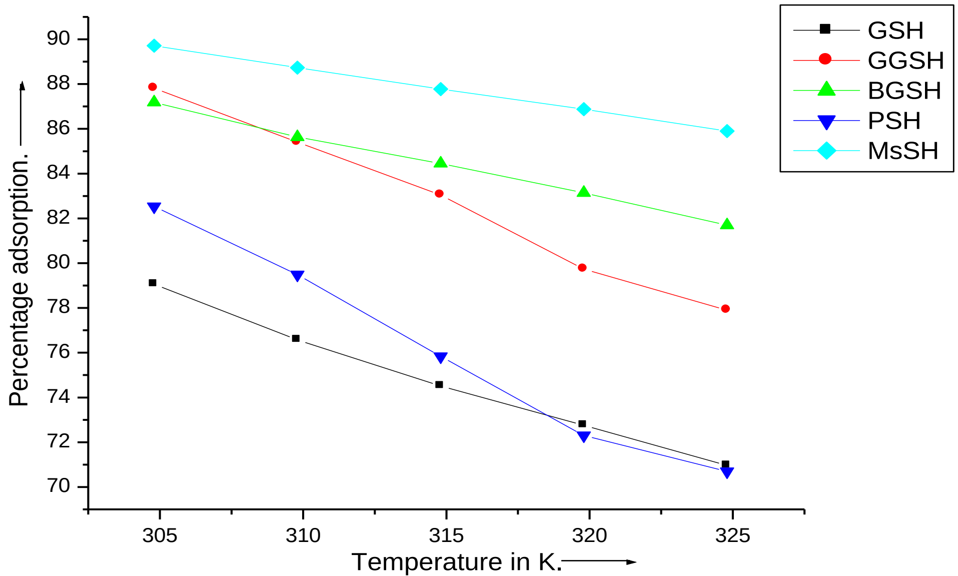

Fig:4.2.4. Effect of temperature on adsorption of MB with adsorbents.

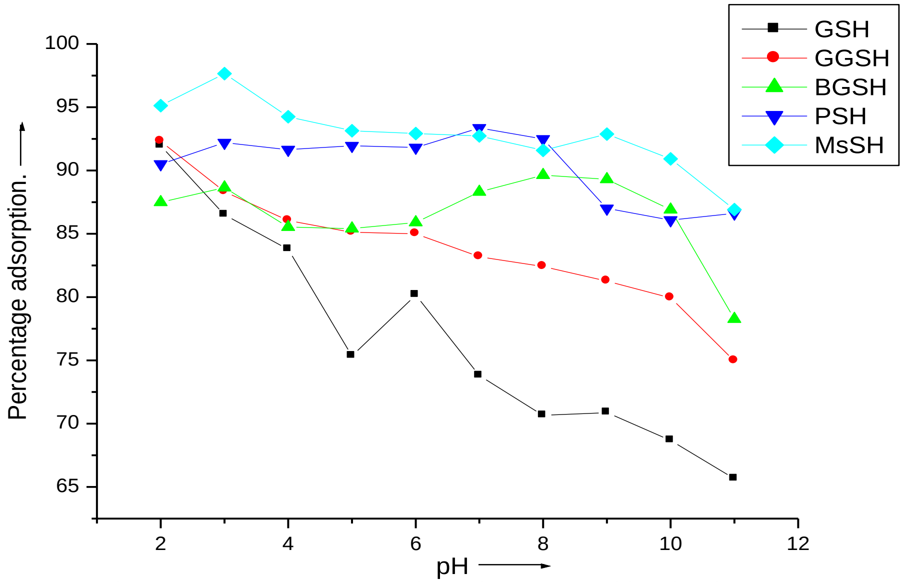

Fig:4.2.5. Effect of pH on adsorption of MB with adsorbents.

4.3 Adsorption study of chromium metal ions on low-cost materials:-

4.3.1 ***Effect of contact time:-*** The various low-cost adsorbents such as GSH, GGSH, BGSH, PSH, MsSH, have been used as a adsorbents for the removal of Cr (VI) metal ions from its aqueous solutions. All solutions were prepared in double distilled water. For each experiment, 50 ml of Cr (VI) solution was continuously stirred with 0.50 gm. 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 $\lambda max = 540$ nm. The effect of contact time, effect of adsorbent dose, initial concentration, effect of temperature, effect of pH, etc. was studied likewise.

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 gm), initial concentration (5 mg/L), pH (5.489) were kept constants. The effect of contact time on Cr (VI) adsorption efficiency showed in Fig. 4.4.1. 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 30 minute. Further increase in contact time did not increased percentage adsorption rapidly. The observed trend of percentage adsorption of Cr (VI) with adsorbents was MsSH>GGSH>GSH> BGSH> PSH.

4.3.2 ***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 gm. The adsorbent was added to 50 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 [35]. The order of percentage adsorption of Cr (VI) metal ion by studied adsorbent forms was MsSH>GGSH> GSH>BGSH> >PSH.

4.3.3 ***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 gm/50 ml) and contact time (24 hours). The experimental results of the initial concentration of Cr (VI) on adsorption efficiency were presented in Fig.4.3.3. The Fig.4.4.3 shows that, the chromium percentage adsorption efficiency increased with the increase in initial concentration of Cr(VI) metal ion solution. The observed trend shows that with adsorbents GSH>GGSH>MsSH>BGSH>PSH.

4.3.4 **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 [36]. Batch adsorption studies were carried out various temperatures 306.5, 311.5, 316.5, 321.5 and 326.5 K. 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.

4.3.5 **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. 4.3.5.. It was observed that the percentage adsorption of Cr (VI) was high in acidic and low in alkaline range. Our results are consistent with those of other workers, who observed that the adsorption of Cr (VI) decreases with increase of pH. The pH dependence of metal adsorption can largely be related to the type and ionic state of the functional groups present on the adsorbent and the metal chemistry in solution [37]. In the pH range 2.0 to 6.0 chromium ions co-exist in different forms, such as $Cr_2O_7^-$, $HCrO_4^-$ $Cr_3O_{10}^-$, of which $HCrO_4^-$ predominates. As the pH of the solution increases, the predominant species become CrO_4^- and $Cr_2O_7^{2-}$, More adsorption at acidic pH suggests that the lower pH results in an increase in H^+ ions associated with the adsorbent surface, resulting in sufficiently strong electrostatic attraction between positively charged adsorbent surface and negatively charged chromate ions. Lesser adsorption of Cr (VI) at pH values greater than 6.0 may be due to the dual competition of both the ions CrO_4^{2-} and OH^- to be adsorbed on the surface of the adsorbent, nothing that OH^- adsorption is favored by higher pH. This is in accordance with the earlier studies that have reported the adsorption of Cr (VI) by different adsorbents [38, 39].

4.3.6 **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 = 0.5 gm. Conc. of adsorbate = 5 ppm.
Volume of adsorbate = 50 ml. pH = 5.489. Temperature = 301.5 ± 0.3 K.

Adsorbents	***Pseudo-first order***			***Pseudo-second order***		
	K_1 (min^{-1})	***q_e (mg/gm)***	***R^2***	***K_2 (gm/mg.min)***	***q_e (mg/gm)***	***R^2***
GSH	$74.341*10^{-3}$	342.019	0.996	$0.268*10^{-3}$	549.450	0.999
GGSH	$83.530*10^{-3}$	175.025	0.987	$0.891*10^{-3}$	510.204	0.999
BGSH	$28.327*10^{-3}$	215.055	0.937	$0.715*10^{-3}$	411.523	0.999
PSH	$6.425*10^{-3}$	183.409	0.903	$0.797*10^{-3}$	74.239	0.986
MsSH	$43.435*10^{-3}$	69.083	0.958	$2.638*10^{-3}$	480.769	0.999

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 [40]. 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 intercept of this line.(Table 4.3.1.) [41] The pseudo second order model is based on the assumption that the rate limiting factor may be chemisorption 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), (q_e) 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 were in the range of 0.996 to 0.903. The observed trend shows that first order kinetics with adsorbents GSH>GGSH>MsSH>BGSH>PSH, while for second order R^2 values are 0.999 to 0.986. The observed trend shows that second order kinetics with adsorbents GSH=GGSH=BGSH=MsSH>PSH. It is clear that the adsorption of Cr (VI) on all adsorbents were 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 [42-44].

4.3.7 <u>Adsorption isotherms:-</u> 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 [45]. The Langmuir isotherm constants, such as adsorption equilibrium *(b) (L/mg),* and the saturated monolayer adsorption capacity *(Q_0) (mg/gm),* 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 = 50 ml.

Temperature = 301.5 ±0.3 K. pH = 7.170 Time = 24 hours.

Adsorbents	***Langmuir constants***				***Freundlich constants***		
	Q_0 (mg/gm.)	***$b* 10^{-5}$ (L/gm.)***	***R_L***	***R^2***	***n***	***K_f (mg/gm(L/gm))$^{1/n}$***	***R^2***
GSH	140.845	1.0925	0.999	0.999	1.002	13.037	0.989
GGSH	14.065	5.631	0.999	0.967	1.024	25.073	0.984
BGSH	434.783	0.258	0.999	0.998	1.020	17.523	0.998
PSH	163.934	0.873	0.999	0.999	1.008	13.941	0.999
MsSH	30.395	0.613	0.999	0.998	1.018	102.471	0.998

The R_L values were for all adsorbents were found to be 0.999. (Table 4.3.2.). Since R_L values obtained are $0 < R_L < 1$ indicates the favorable adsorption of Cr (VI) metal ions by all adsorbents 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 [46-50]. 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 $log\, C_e$ [51, 52]. The *n* values were for adsorbents from 1.002 to 1.024. The observed trend shows that with adsorbents GGSH>BGSH>MsSH>PSH>GSH. (Table 4.4.3.). The values of n greater than unity, *(1< n <10)*, that means favorable adsorption [53-56].

4.3.8 <u>Thermodynamics of adsorption</u>:- Thermodynamic parameters such as Gibb's free energy change ΔG^0, enthalpy change ΔH^0 and entropy change ΔS^0 were calculated at different temperatures usin Van't Hoff's equation.

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

Conc. of adsorbate = 5 ppm. Volume of adsorbate = 50 ml.

Amount of adsorbent = 0.5 gm. pH = 6.5 Time = 24 hours.

Temp (K)	Free energy change *($\Delta G°$)* of Chromium [Cr (VI)] metal ion solution at different adsorbent with different temperature in KJ/mole.				
	GSH	*GGSH*	*BGSH*	*PSH*	*MsSH*
306.5	-9.461	-8.703	-7.670	-0.873	-8.535
311.5	-8.703	-8.414	-7.377	-0.263	-8.168
316.5	-7.945	-8.126	-7.084	0.347	-7.802
321.5	-7.187	-7.837	-6.791	0.956	-7.436

326.5	-6.429	-7.548	-6.498	1.566	-7.070

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 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 [57, 58]. The values of ΔH^0 were for adsorbents in the range -55.925 to - 20.171 KJ/mole. The observed trend shows that GSH>PSH>MsSH>GGSH>BGSH. The negative value of ΔH^0 suggests that the adsorption is exothermic. The values of ΔS^0 were for adsorbents in the range -151.60 to -38.940 J/mole. The observed trend shows that GSH> PSH> MsSH>BGSH>GGSH. The negative value of ΔS^0 suggests that the decreased disorder and randomness at the solid solution interface with adsorption.

Table: 4.3.4. Thermodynamic parameter values with Cr (VI) metal ion solution:-

Conc. of adsorbate = 5 ppm. Volume of adsorbate = 50 ml.
Amount of adsorbent = 0.5 gm. pH = 6.5 Time = 24 hours.

Thermodynamic parameters	ΔH° and ΔS° values of Chromium [Cr (VI)] metal ion at different adsorbent.				
	GSH	*GGSH*	*BGSH*	*PSH*	*MsSH*
$-\Delta H°$ KJ/mole	55.925	26.410	25.627	38.249	30.985
$-\Delta S°$ J/mole	151.60	57.770	58.590	121.95	73.25

4.3.9 Conclusion:- 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 were fitted using different two isotherm models, Langmuir and Freundlich, which were in good agreement with the experimental data. Adsorption of Cr (VI) was found to increase with increase in time, adsorbent dose and initial concentration and decreased with increase in temperature. The adsorption of Cr (VI) decreases with increase of pH. 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 GSH, GGSH, BGSH, PSH, and MsSH can be used as potential low cost adsorbents for the adsorption of Cr (VI) from aqueous solutions over a wide range of concentrations. The GSH, GGSH, BGSH, PSH, and MsSH adsorbents had been proved as one of the efficient adsorbents for the adsorption of Cr (VI) from industrial wastewater. They were identified to be an effective adsorbent for the adsorption of Cr (VI) from aqueous solution. Also, adsorbents can be used to adsorbed heavy metal ions and organic pollutants.

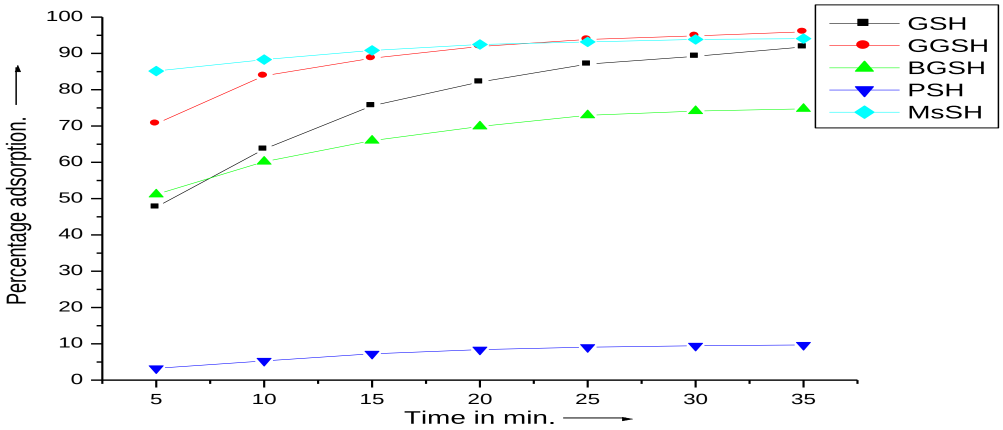

Fig:4.3.1. Effect of contact time on adsorption of Cr(VI) with adsorbents.

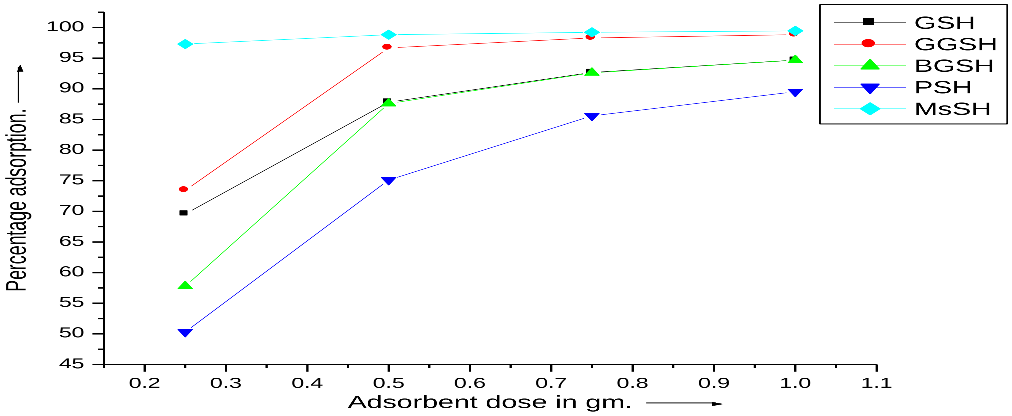

Fig:4.3.2. Effect of adsorbent dose on adsorption of Cr(VI) with adsorbents.

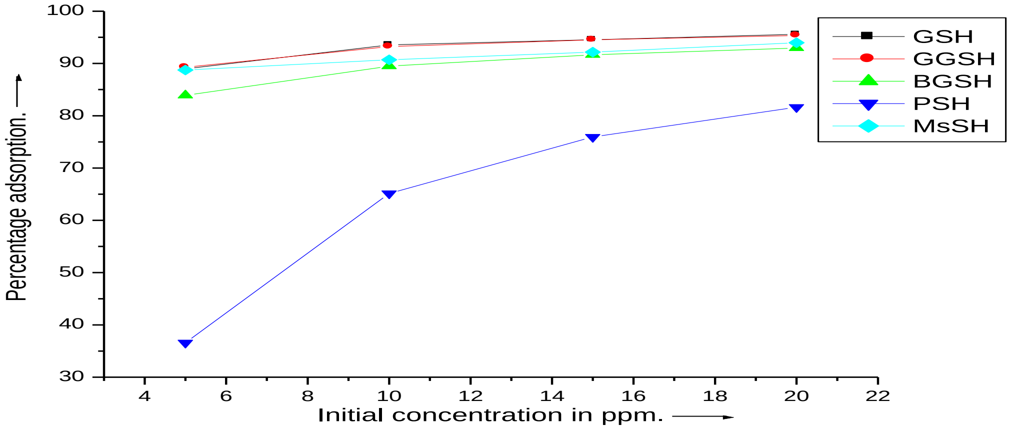

Fig:4.3.3. Effect of initial concentration on adsorption of Cr(VI) with adsorbents.

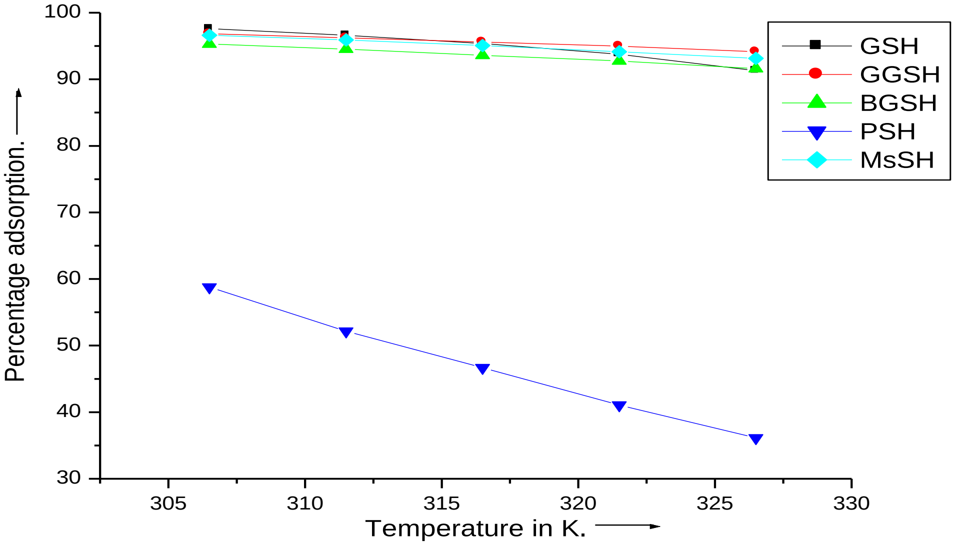

Fig:4.3.4. Effect of temperature on adsorption of Cr(VI) with adsorbents.

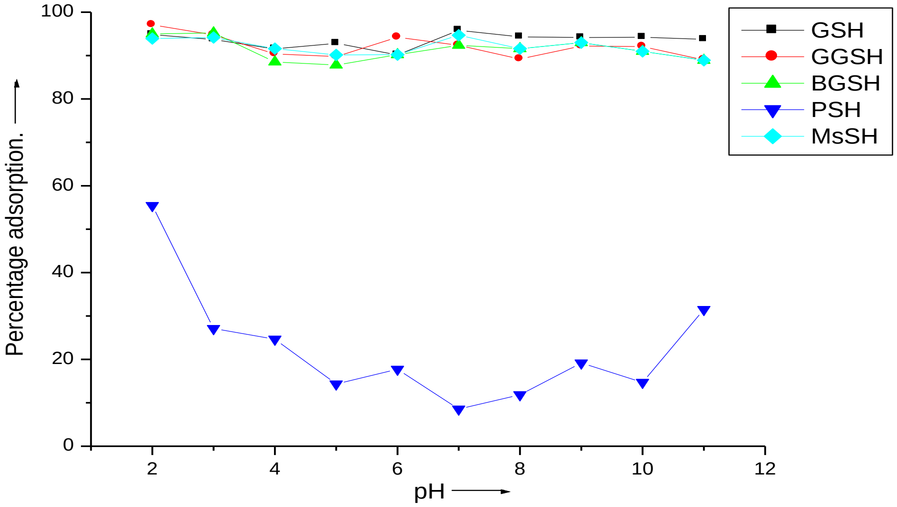

Fig:4.3.5. Effect of pH on adsorption Of Cr(VI) with adsorbents.

4.4 Adsorption study of nickel metal ions on low-cost materials:-

4.4.1 ***Effect of contact time:-*** The adsorption experiments were carried out in stirred batch mode to perform the experiment, working solution of Ni (II) was prepared by dissolving the respective metal sulfate in double distilled water, the GSH, GGSH, BGSH, PSH, and MsSH powders were used as adsorbents for adsorption of Ni (II) metal ions. The residual were withdrawn at appropriate time intervals and filtered; the absorbance of supernant liquid was determined at λmax = 366 nm. The effect of contact time, effect of adsorbent dose, initial concentration, effect of temperature, effect of pH, etc. was studied.

Effect of contact time on the adsorption of Ni (II) metal ion on the adsorbents such as GSH, GGSH, BGSH, PSH, and MsSH was carried out using batch technique. The results for the effect of contact time on the adsorption of Ni (II) metal ion adsorption are shown in Fig.4.4.1. 0.5 gm of adsorbent, and 20 mg/L concentration were used for this experiment in contact time 35 minute at temperature 303.0 ± 0.3 K. It is noted that the rate of percentage adsorption of Ni metal ions increases with increase in contact time. At the initial stage rate of percentage adsorption of Ni (II) metal ion was higher due to availability of large number of active sites on the surface of the adsorbent and becomes slower after 30 minutes, due to decreased number of active sites. The maximum adsorption of Ni (II) found on BGSH adsorbent, while minimum on GSH adsorbent. The observed trend shows that BGSH>PSH>MsSH>GGSH>GSH. Similar observation has been reported in literature [59].

4.4.2 ***Effect of adsorbent dose:-***The effect of adsorbent dose on the adsorption of Ni (II) metal ion was studied by using different masses of the adsorbent in the range of 0.25 to 1.0 gm. The percentage adsorption of Ni (II) metal ion increases with increase in adsorption dose.(Fig. 4.4.2.), this is because of the availability of more and more binding sites for complexion of Ni (II) metal ions.

4.4.3 ***Effect of initial concentration:-*** A series of experiments were studied for the effect of initial concentration on the adsorption of NI (II) metal ions by adsorbents such as GSH, GGSH, BGSH, PSH, and MsSH. The initial concentration of Ni (II) metal ion was varied from 5 to 20 mg/L, keeping all other parameters at their optimum levels. The graph presented in Fig.4.4.3.showed that the percentage adsorption of Ni (II) metal ion capacity increased with increase in the Ni (II) metal concentration. This was due to higher probabilities of collision between metal ion and adsorbent. The observed trend showed that with adsorbents GSH>MsSH>GGSH> PSH>BGSH. Similar observation was reported in literature [60].

4.4.4 ***Effect of temperature:-***Effect of temperature on Ni (II) metal ions adsorption was evaluated at temperatures of 306.5, 311.5, 316.5, 321.5 and 326.5 K., the other parameters were kept constants (Table 3.6.4. (a)- 3.6.4.(i)). The effect of temperature on the percentage adsorption of NI (II) metal ion on adsorbents was shown in Fig. 4.4.4. The result reveals that the percentage adsorption of Ni (II) metal ion decreases with increase in temperature, indicating that the adsorption is exothermic.

4.4.5 ***Effect of pH:-*** pH is also an important parameter that affects the adsorption of Ni (II) metal ions from aqueous solution. The batch adsorption studies at different pH values were carried out in the range of 2.00 to 11.00. The results are shown in Fig.4.4.5. The maximum percentage adsorption of Ni (II) metal ions was observed at pH 6.0 and hence this was taken as the optimum pH for subsequent studies. The percentage adsorption of Ni (II) metal ions increased rapidly at pH 3.00 to 6.00. At lower pH value, the H^+ ions compete with Ni (II) metal cations for the surface of the adsorbent which we hinder Ni (II) metal ion s from reaching the binding the sites of the adsorbent caused by repulsive forces. Decrease the percentage adsorption Ni (II) metal ions at higher pH due to the formation of soluble hydroxide complexes. The Ni metal cations are completely released under circumstances of extreme acidic conditions.[61].

4.4.6 ***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.

Table: 4.4.1. Kinetic parameter values with Nickel [Ni (II)] metal ion:-
Amount of adsorbent = 0.5 gm. Conc. of adsorbate = 20 ppm.
Volume of adsorbate = 50 ml. pH = 5.889 Temperature = 303.0 ± 0.3 K.

Adsorbents	***Pseudo-First order***			***Pseudo-first order***		
	K₁ (min⁻¹)	***q_e (mg/gm)***	***R^2***	***K₂ (gm/mg.min)***	***q_e (mg/gm)***	***R^2***
GSH	$40.763*10^{-3}$	124.721	0.994	$1.508*10^{-3}$	1541.632	0.999
GGSH	$39.842*10^{-3}$	124.371	0.998	$1.502*10^{-3}$	1541.383	0.999
BGSH	$53.798*10^{-3}$	132.294	0.997	$1.371*10^{-3}$	1552.981	0.999
PSH	$38.759*10^{-3}$	180.884	0.992	$1.017*10^{-3}$	1581.008	0.999
MsSH	$28.718*10^{-3}$	149.012	0.947	$1.499*10^{-3}$	1560.420	0.999

The rate constants, the correlation coefficients *(R^2)* and calculated q_e for all adsorbents are in table 4.4.1, the values of *(R^2)* with first order were in the range of 0.999 to 0.947. The observed trend shows that with adsorbents for first order kinetics GGSH>BGSH>GSH>PSH>MsSH, while for second order *(R^2)* value was 0.999 for all adsorbents. The values of (R^2) obtained from pseudo second-order model were higher than pseudo first-order model, indicating that the adsorption process followed the pseudo second-order model for entire adsorption period [62, 63].

4.4.7 **Adsorption isotherm:-** In order ro investigate how Ni (ii) interacts with adsorbents, the Langmuir and Freundlich isotherm models were applied (Table 4.4.2.). The Langmuir isotherm has been used by various workers for the adsorption study of a variety of compounds [64]. The values of the Langmuir constants are calculated from the intercept and slope of a the plot of C_e/q_e against C_e and calculate the essential characteristics of Langmuir isotherm model, which can be explained in terms of separation factor (R_L), which was used to predict whether the adsorption system is "favorable" of "unfavorable", if R_L value is in the range of $0 < R_L < 1$, which indicates that the adsorption is favorable. Since R_L values lies between 0 to 1 for Ni (II) metal ion studies, it seen that the adsorption of Ni (II) metal ion is favorable. The data reveal that the Langmuir model yields better fit than the Freundlich model.

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

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

Temperature = 306.5 ±0.3 K. pH = 5.7 Time = 24 hours.

Adsorbents	***Langmuir constants***				***Freundlich constants***		
	Q_0 (mg/gm.)	$b \times 10^{-3}$ (L/gm.)	R_L	R^2	n	K_f $(mg/gm(L/gm))^{1/n}$	R^2
GSH	851.4914	0.009	0.999	0.999	1.144	17.4080	0.999
GGSH	357.8330	0.020	0.998	0.999	1.210	17.3972	0.998
BGSH	404.7157	0.019	0.998	0.999	1.171	17.8649	0.999
PSH	411.2603	0.020	0.998	0.999	1.150	18.3434	0.999
MsSH	141.1769	0.064	0.993	0.997	1.317	20.0812	0.997

The obtained range of R_L values for adsorbents are 0.999 to 0.993.; the observed trend showed that with adsorbents GSH>GGSH=BGSH=PSH>MsSH. The Freundlich isotherm model that can be used for non-ideal adsorption process, involves heterogeneous adsorption surface and active sites with different energies, when plotted as the data are of $\log\frac{x}{m}$ against $\log C_e$, 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 [65]. The values of n has calculated and presented in Table:4.4.2. The values were found to be between 1 and 10, this indicates favorable adsorption. The result shows that the adsorption of NI (II) metal ion follows Langmuir and Freundlich isotherm model. The n values were for adsorbents from 1.317 to 1.135; the observed trend showed that with adsorbents MsSH>GGSH>BGSH>PSH>GSH.

4.4.8 **Thermodynamics of adsorption:-** 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: 4.4.3. Free energy change $(\Delta G°)$ of Ni (II) metal ion solution at diffent temp.:-
Conc. of adsorbate = 20 ppm. Volume of adsorbate = 50 ml.
Amount of adsorbent = 0.5 gm. pH = 5.7 Time = 24 hours.

Temp (K)	Free energy change $(\Delta G°)$ of Nickel [Ni (II)] metal ion solution at different adsorbent with different temperature in KJ/mole.				
	GSH	*GGSH*	*BGSH*	*PSH*	*MsSH*
306.5	-3.855	-2.992	-2.955	-3.569	-3.919
311.5	-3.749	-2.992	-2.964	-3.469	-3.835
316.5	-3.643	-2.992	-2.972	-3.370	-3.752
321.5	-3.537	-2.992	-2.981	-3.270	-3.668
326.5	-3.431	-2.992	-2.989	-3.171	-3.585

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 Ni (II) metal ions are < -10 KJ/mole, which indicate that physical adsorption 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 [66, 67]. 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 values of ΔH^0 were for adsorbents in the range -25.844 to -3.228 KJ/mole. In this present study, ΔH^0 was found to be less than -40 KJ/mole. This indicates physical adsorption and adsoebate-substrate bond is long as compared with the length of covalent or ionic bond. The observed trend shows that BGSH>GSH>PSH>MsSH >GGSH. The negative value of ΔH^0 suggests that the adsorption is exothermic. The values of ΔS^0 were for adsorbents in the range -25.301 to -0.940 J/mole. The observed trend shows that GSH>PSH>MsSH>BGSH>GGSH. The negative value of ΔS^0 suggests that the decreased disorder and randomness at the solid solution interface with adsorption.

Table: 4.4.4. Thermodynamic parameter values with Nickel metal ion solution:-
Conc. of adsorbate = 20 ppm. Volume of adsorbate = 50 ml.
Amount of adsorbent = 0.5 gm. pH = 5.7 Time = 24 hours.

Thermodynamic parameters	$\Delta H°$ and $\Delta S°$ values of Nickel [Ni (II)] metal ion at different adsorbent.				
	GSH	*GGSH*	*BGSH*	*PSH*	*MsSH*
$-\Delta H°$ KJ/mole	11.008	3.2285	25.844	9.556	9.087
$-\Delta S°$ J/mole	23.184	0.940	1.213	19.503	16.938

4.4.9 **Conclusion:-** The experiments for the removal of Ni (II) metal ion from aqueous solution have been carried out using GSH, GGSH, BGSH, PSH, and MsSH low-cost adsorbents, it had been examined at different pH values, contact time, adsorbent dose, initial metal ion concentration, and temperature. The maximum adsorption of Ni (II) metal ion is obtained at an acidic pH of 6.0 Under our experimental conditions; the results were fitted to various, kinetic, isotherm and thermodynamic equations to determine the best mechanisms and correlate the experimental data. The kinetic study of the adsorption of Ni (II) metal ion showed that the pseudo-second order kinetic model provides better correlation of the adsorption data than the pseudo-first order kinetic model. The adsorption isotherms were described by Langmuir and Freundlich; the present work investigate that the adsorption of Ni (II) metal ion followed both the Langmuir and Freundlich adsorption isotherms. The percentage adsorption efficiency of Ni (II) metal ion increased with increasing adsorbent dosage, contact time, initial concentration of Ni (II) metal ion solution while was decreased with increasing temperature. The Ni (II) metal ion adsorption equilibrium was attained after 24 hours. The thermodynamic parameters such as Gibb's free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) studies indicates that, the negative values of ΔG^0 indicated the spontaneous nature of adsorption, physical adsorption and confirmed affinity of adsorbents for the Ni (II) metal ion. Negative value of ΔH^0 confirmed the exothermic nature of the adsorption process. The investigation showed that all adsorbents were agricultural waste, abundant, cheap, readily available and environment-friendly effective adsorbent, which could be used as potential adsorbent for adsorption of Ni (II) metal ion from aqueous solution and polluted water.

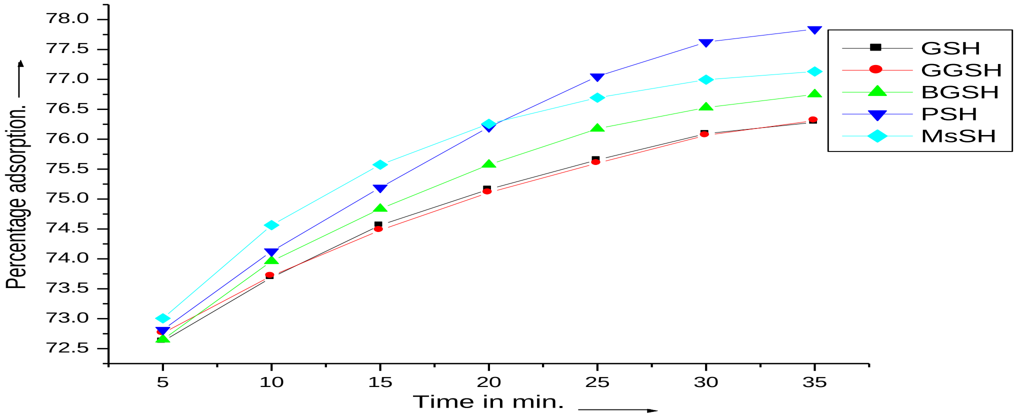

Fig:4.4.1. Effect of contact time on adsorption of Ni (II) with adsorbents.

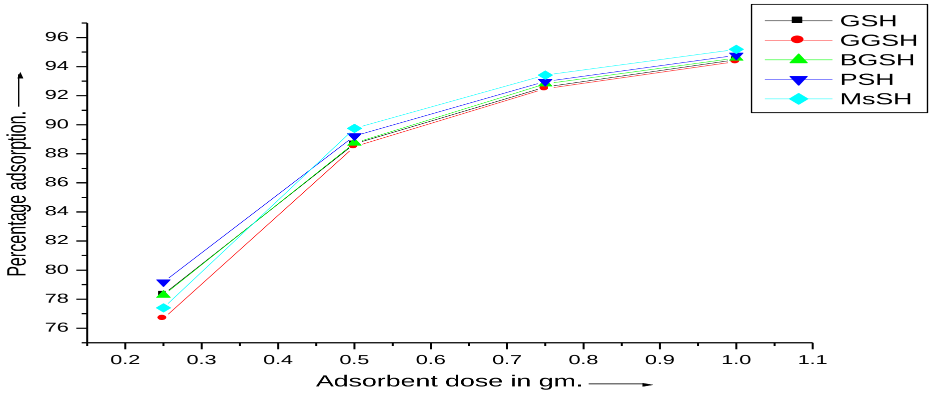

Fig:4.4.2. Effect of adsorbent dose on adsorption of Ni (II) with adsorbents.

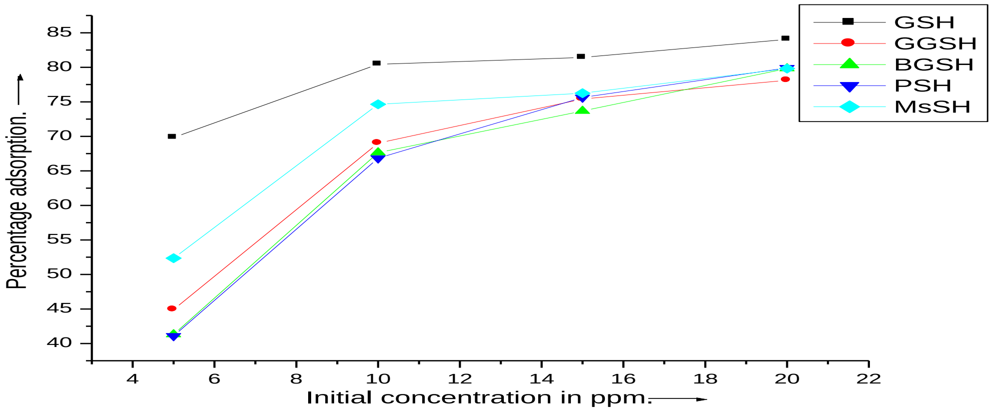

Fig:4.4.3. Effect of initial concentration on adsorption of Ni (II) with adsorbents.

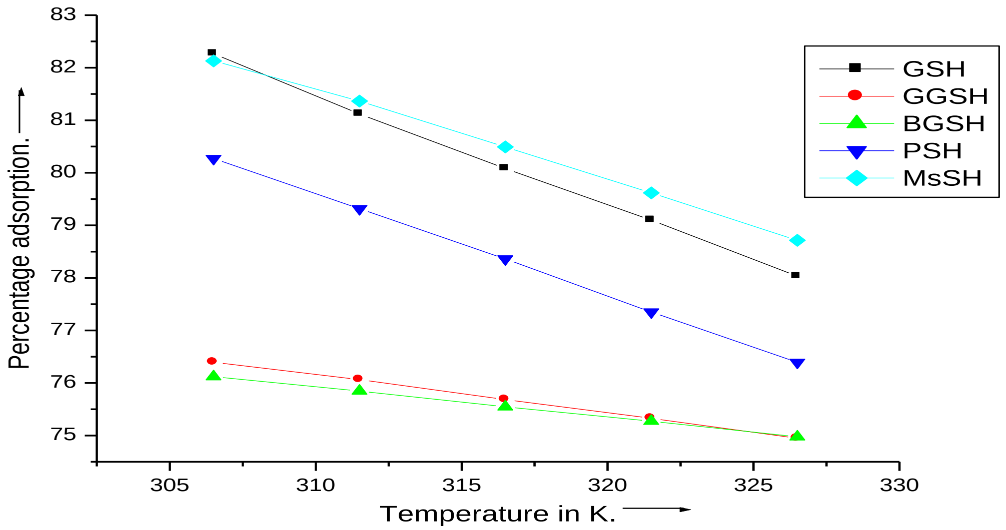

Fig:4.4.4. Effect of temperature on adsorption of Ni (II) with adsorbents.

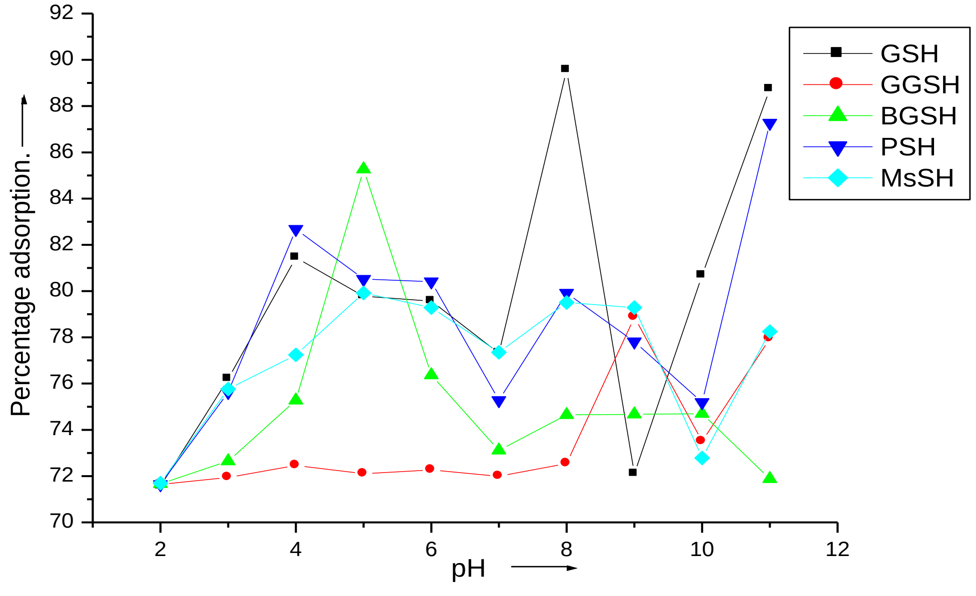

Fig:4.4.5. Effect of pH on adsorption of Ni (II) with adsorbents.

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Husk of gram seeds as a low –cost adsorbent for the removal of methylene blue dye from aqueous solutions

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Methylene blue dye adsorption on agricultural waste (husk of gram seeds) has been studied through batch experiments. The effect of different parameters such as contact time, initial dye concentration, adsorbent dosage, effect of salt & effect of temperature were investigated. It was observed that the adsorption increases with increase in temperature. The result show that husk of gram seeds could be employed effective & low cost material for adsorption of dye from aqueous solutions.

Key words: Methylene blue, husk of gram seeds, adsorption, freundlich isotherm, langmuir isotherm.

INTRODUCTION

Discharge of effluents from several industries is chief of sources of dye contamination of water. Decolourization of dyes is important aspects of waste water treatment before discharge (Sarioglu and Atay, 2006). Decolourization of dyes in aquatic environment is difficult because dyes are not easily degradable & are generally not removed from waste water by conventional waste water system.

Thus the simple & inexpensive procedure for their removal highly demanded. Several techniques have been used for the treatment of waste water contaminated with organic dyes, but only at low concentrations of chemical contaminants. Though the methods like ultra filtration, electrochemical adsorption, photo oxidation, chemical precipitation (Kannan and Sundaram, 2001; Bhattacharyya and Sharma, 2005). etc. are efficient, but adsorption is a widely used for removal of different contaminants from waste water (Walker and Weatherley, 1998; Urbain et al., 2013). This method is efficient and inexpensive so can be operated at large scale.

Adsorption process has been exclusively exploited for the removal of toxic chemical from waste water. Commercial Activated Carbon (CAC) is commonly used for dye removal; however, its expensiveness & the regeneration or disposal is the problems associated with it. Successful application of adsorption technique demands innovation of cheap, non-toxic, and locally available adsorbent. Thus low cost biodegradable adsorbents like agricultural bio-materials have received considerable attention for colour removal from waste waters as it offers the most economical & effective option. Bio-material adsorbents like bagasse (Urbain et al., 2013), sawdust (Sayyed et al., 2013; Abdeen, 2012), rice husk(Dar et al., 2013), coconut coir (Dar et al., 2012), banana pith (APHA, 1995), used tea leaves & cowdung (Vogel, 1969), have been found to be highly effective , cheap & biologically safe adsorbents. Keeping this in view we tried to know the adsorption capacity of husk of gram seeds (Al-Qodah, 2000) (*Cicer arientinum*).

Cicer arientinum is abundantly cultivated in India and contains high protein content. It is one of the earlier cultivated vegetables and needs subtropical or tropical climates with more than 400 millimetres of annual rain. It can be grown in temperate climate but yields will be much lower. Shed down husk from pulses are of little use so we decided to turn such waste material in to a beneficial one.

EXPERIMENTAL

The adsorption experiments were carried out in a batch

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Research Article

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Adsorption studies of chromium (VI) ion from aqueous solution using *Pisum sativum*

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Abstract

The use of *Pisum sativum* seed husk as low-cost adsorbents was investigated for the replacement for currently costly methods of adsorption Cr(VI) ions from aqueous solutions. Batch adsorption studies showed that *Pisum sativum* seed husk was able to adsorb Cr(VI) ions from aqueous solution. The effect of contact time, effect of initial concentration, effect of adsorbent dose, etc. have been reported. Equilibrium data were analyzed using the Langmuir Freundlich isotherms whereas the adsorption kinetic data were evaluated by the pseudo-first-order and pseudo-second-order kinetic models. The results obtained indicate that the adsorption of Cr(VI) on *Pisum sativum* seed husk is maximum at 20 mg/L metal ion concentration and 1.0 gm. adsorbent dose. The results demonstrated that *Pisum sativum* seed husk have potential to be employed as the adsorbent for the adsorption of Cr (VI) metal ions from aqueous solution.

Keywords: Chromium, *Pisum sativum* seed husk, adsorption, isotherm, aqueous solution, kinetics, thermo-dynamic parameters.

Contents

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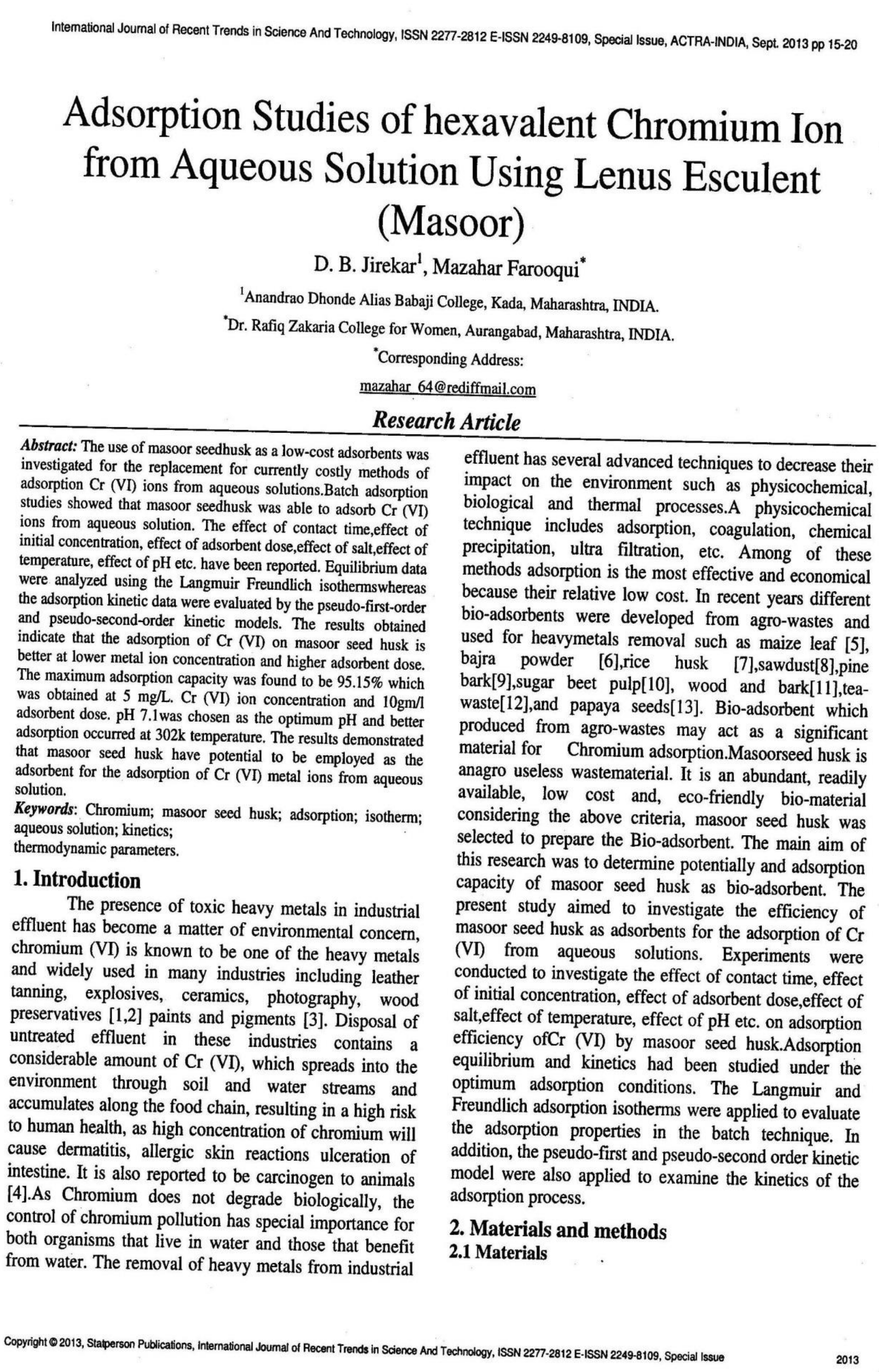
1. Introduction

The presence of toxic heavy metals in industrial effluent has become a matter of environmental concern, chromium (VI) is known to be one of the heavy metals and widely used in many industries including leather tanning, explosives, ceramics, photography, wood preservatives [1,2] paints and pigments [3]. Disposal of untreated effluent in these industries contains a considerable amount of Cr (VI), which spreads into the environment through soil and water streams and accumulates along the food chain, resulting in a high risk to human health, as high concentration



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Adsorption Studies of hexavalent Chromium Ion from Aqueous Solution Using Lenus Esculent (Masoor)

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Research Article

Abstract: The use of masoor seedhusk as a low-cost adsorbents was investigated for the replacement for currently costly methods of adsorption Cr (VI) ions from aqueous solutions.Batch adsorption studies showed that masoor seedhusk was able to adsorb Cr (VI) ions from aqueous solution. The effect of contact time,effect of initial concentration, effect of adsorbent dose,effect of salt,effect of temperature, effect of pH etc. have been reported. Equilibrium data were analyzed using the Langmuir Freundlich isothermswhereas the adsorption kinetic data were evaluated by the pseudo-first-order and pseudo-second-order kinetic models. The results obtained indicate that the adsorption of Cr (VI) on masoor seed husk is better at lower metal ion concentration and higher adsorbent dose. The maximum adsorption capacity was found to be 95.15% which was obtained at 5 mg/L. Cr (VI) ion concentration and 10gm/l adsorbent dose. pH 7.1was chosen as the optimum pH and better adsorption occurred at 302k temperature. The results demonstrated that masoor seed husk have potential to be employed as the adsorbent for the adsorption of Cr (VI) metal ions from aqueous solution.

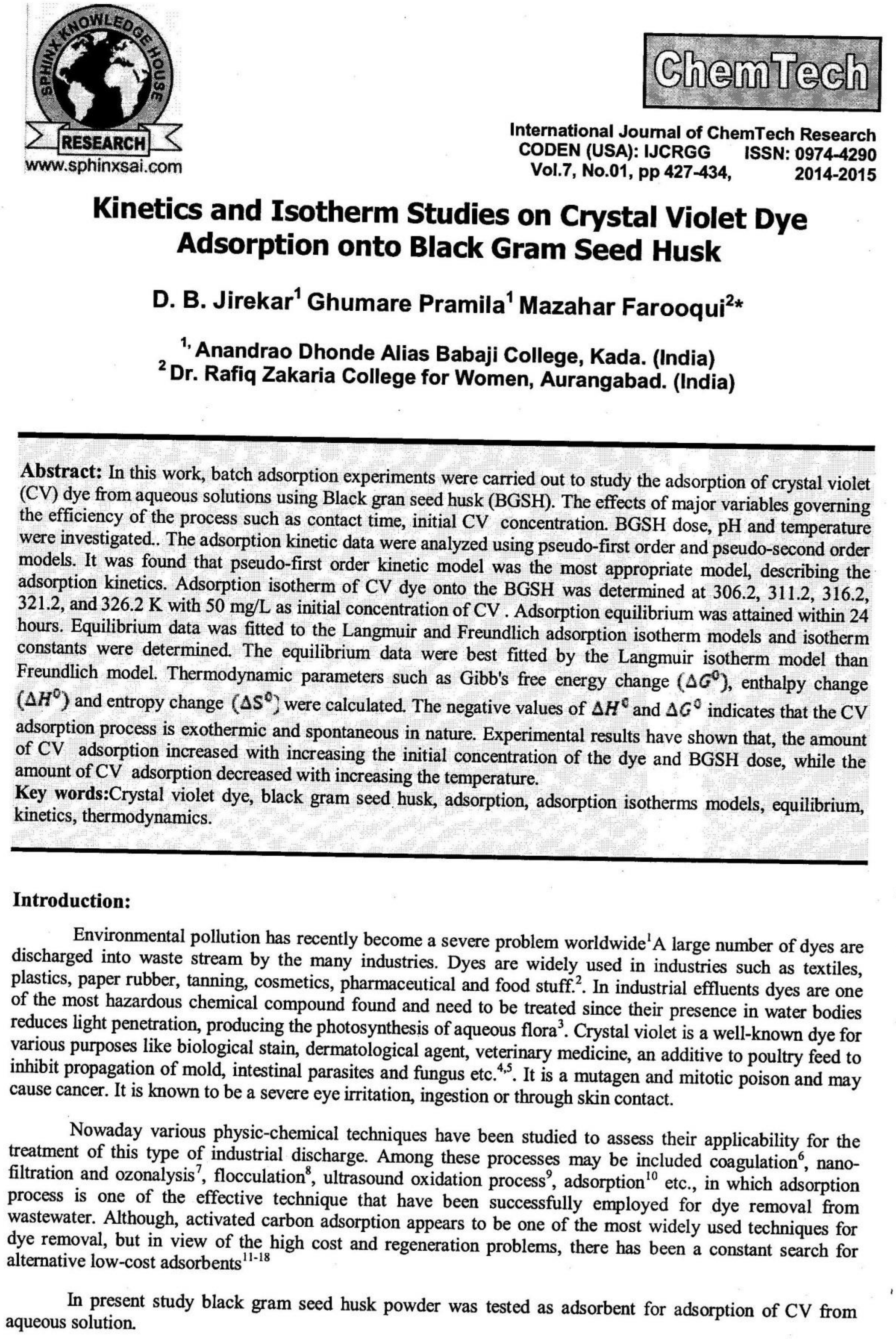
Keywords: Chromium; masoor seed husk; adsorption; isotherm; aqueous solution; kinetics;
thermodynamic parameters.

1. Introduction

The presence of toxic heavy metals in industrial effluent has become a matter of environmental concern, chromium (VI) is known to be one of the heavy metals and widely used in many industries including leather tanning, explosives, ceramics, photography, wood preservatives [1,2] paints and pigments [3]. Disposal of untreated effluent in these industries contains a considerable amount of Cr (VI), which spreads into the environment through soil and water streams and accumulates along the food chain, resulting in a high risk to human health, as high concentration of chromium will cause dermatitis, allergic skin reactions ulceration of intestine. It is also reported to be carcinogen to animals [4].As Chromium does not degrade biologically, the control of chromium pollution has special importance for both organisms that live in water and those that benefit from water. The removal of heavy metals from industrial effluent has several advanced techniques to decrease their impact on the environment such as physicochemical, biological and thermal processes.A physicochemical technique includes adsorption, coagulation, chemical precipitation, ultra filtration, etc. Among of these methods adsorption is the most effective and economical because their relative low cost. In recent years different bio-adsorbents were developed from agro-wastes and used for heavymetals removal such as maize leaf [5], bajra powder [6],rice husk [7],sawdust[8],pine bark[9],sugar beet pulp[10], wood and bark[11],tea-waste[12],and papaya seeds[13]. Bio-adsorbent which produced from agro-wastes may act as a significant material for Chromium adsorption.Masoorseed husk is anagro useless wastematerial. It is an abundant, readily available, low cost and, eco-friendly bio-material considering the above criteria, masoor seed husk was selected to prepare the Bio-adsorbent. The main aim of this research was to determine potentially and adsorption capacity of masoor seed husk as bio-adsorbent. The present study aimed to investigate the efficiency of masoor seed husk as adsorbents for the adsorption of Cr (VI) from aqueous solutions. Experiments were conducted to investigate the effect of contact time, effect of initial concentration, effect of adsorbent dose,effect of salt,effect of temperature, effect of pH etc. on adsorption efficiency ofCr (VI) by masoor seed husk.Adsorption equilibrium and kinetics had been studied under the optimum adsorption conditions. The Langmuir and Freundlich adsorption isotherms were applied to evaluate the adsorption properties in the batch technique. In addition, the pseudo-first and pseudo-second order kinetic model were also applied to examine the kinetics of the adsorption process.

2. Materials and methods

2.1 Materials



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Kinetics and Isotherm Studies on Crystal Violet Dye Adsorption onto Black Gram Seed Husk

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Abstract: In this work, batch adsorption experiments were carried out to study the adsorption of crystal violet (CV) dye from aqueous solutions using Black gran seed husk (BGSH). The effects of major variables governing the efficiency of the process such as contact time, initial CV concentration. BGSH dose, pH and temperature were investigated.. The adsorption kinetic data were analyzed using pseudo-first order and pseudo-second order models. It was found that pseudo-first order kinetic model was the most appropriate model, describing the adsorption kinetics. Adsorption isotherm of CV dye onto the BGSH was determined at 306.2, 311.2, 316.2, 321.2, and 326.2 K with 50 mg/L as initial concentration of CV . Adsorption equilibrium was attained within 24 hours. Equilibrium data was fitted to the Langmuir and Freundlich adsorption isotherm models and isotherm constants were determined. The equilibrium data were best fitted by the Langmuir isotherm model than Freundlich model. Thermodynamic parameters such as Gibb's free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated. The negative values of ΔH^0 and ΔG^0 indicates that the CV adsorption process is exothermic and spontaneous in nature. Experimental results have shown that, the amount of CV adsorption increased with increasing the initial concentration of the dye and BGSH dose, while the amount of CV adsorption decreased with increasing the temperature.

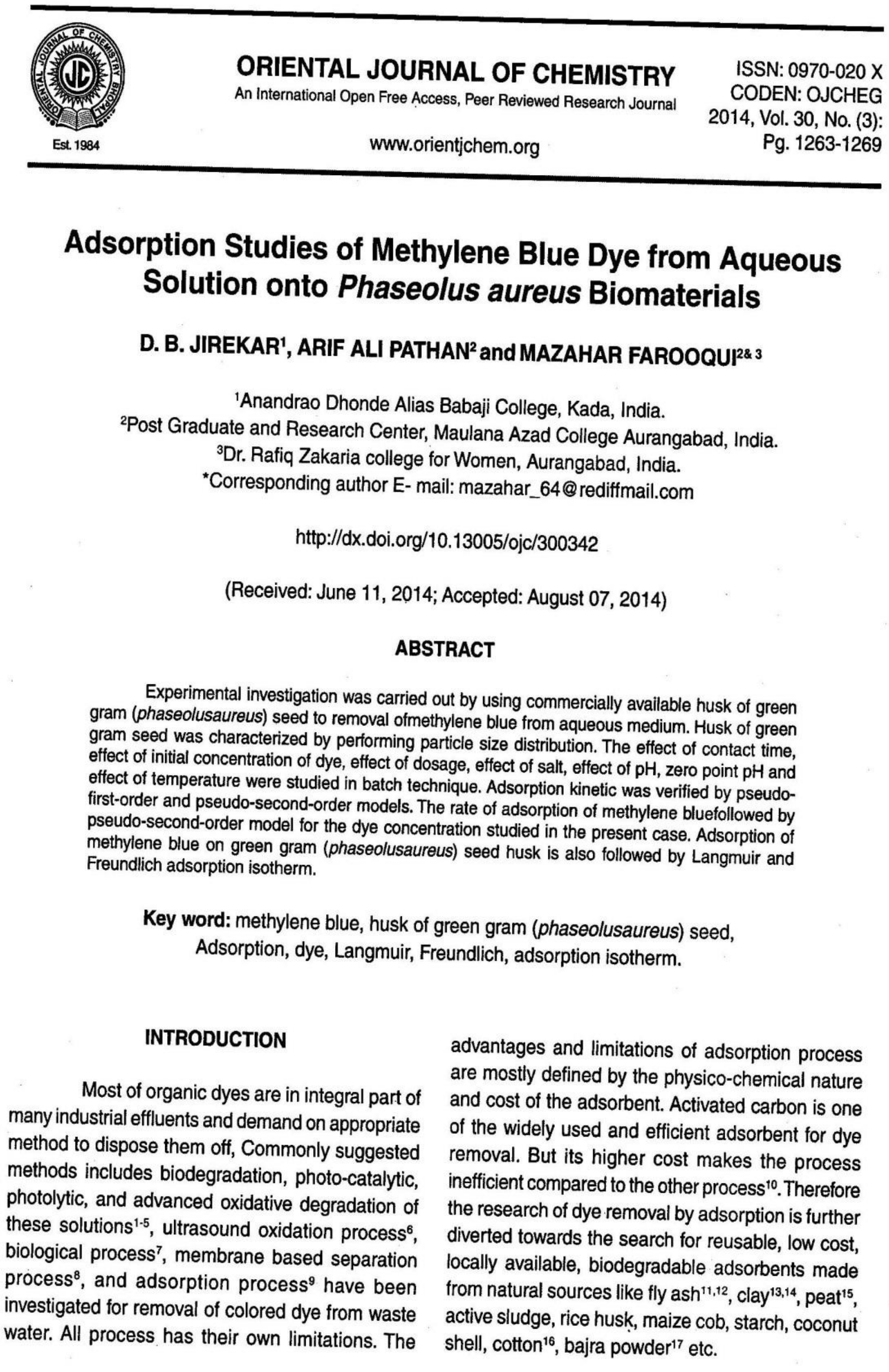
Key words: Crystal violet dye, black gram seed husk, adsorption, adsorption isotherms models, equilibrium, kinetics, thermodynamics.

Introduction:

Environmental pollution has recently become a severe problem worldwide[1]A large number of dyes are discharged into waste stream by the many industries. Dyes are widely used in industries such as textiles, plastics, paper rubber, tanning, cosmetics, pharmaceutical and food stuff.[2]. In industrial effluents dyes are one of the most hazardous chemical compound found and need to be treated since their presence in water bodies reduces light penetration, producing the photosynthesis of aqueous flora[3]. Crystal violet is a well-known dye for various purposes like biological stain, dermatological agent, veterinary medicine, an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus etc.[4,5]. It is a mutagen and mitotic poison and may cause cancer. It is known to be a severe eye irritation, ingestion or through skin contact.

Nowaday various physic-chemical techniques have been studied to assess their applicability for the treatment of this type of industrial discharge. Among these processes may be included coagulation[6], nano-filtration and ozonalysis[7], flocculation[8], ultrasound oxidation process[9], adsorption[10] etc., in which adsorption process is one of the effective technique that have been successfully employed for dye removal from wastewater. Although, activated carbon adsorption appears to be one of the most widely used techniques for dye removal, but in view of the high cost and regeneration problems, there has been a constant search for alternative low-cost adsorbents[11-18]

In present study black gram seed husk powder was tested as adsorbent for adsorption of CV from aqueous solution.



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Adsorption Studies of Methylene Blue Dye from Aqueous Solution onto *Phaseolus aureus* Biomaterials

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ABSTRACT

Experimental investigation was carried out by using commercially available husk of green gram (*phaseolusaureus*) seed to removal ofmethylene blue from aqueous medium. Husk of green gram seed was characterized by performing particle size distribution. The effect of contact time, effect of initial concentration of dye, effect of dosage, effect of salt, effect of pH, zero point pH and effect of temperature were studied in batch technique. Adsorption kinetic was verified by pseudo-first-order and pseudo-second-order models. The rate of adsorption of methylene bluefollowed by pseudo-second-order model for the dye concentration studied in the present case. Adsorption of methylene blue on green gram (*phaseolusaureus*) seed husk is also followed by Langmuir and Freundlich adsorption isotherm.

Key word: methylene blue, husk of green gram (*phaseolusaureus*) seed, Adsorption, dye, Langmuir, Freundlich, adsorption isotherm.

INTRODUCTION

Most of organic dyes are in integral part of many industrial effluents and demand on appropriate method to dispose them off, Commonly suggested methods includes biodegradation, photo-catalytic, photolytic, and advanced oxidative degradation of these solutions[1-5], ultrasound oxidation process[6], biological process[7], membrane based separation process[8], and adsorption process[9] have been investigated for removal of colored dye from waste water. All process has their own limitations. The advantages and limitations of adsorption process are mostly defined by the physico-chemical nature and cost of the adsorbent. Activated carbon is one of the widely used and efficient adsorbent for dye removal. But its higher cost makes the process inefficient compared to the other process[10]. Therefore the research of dye removal by adsorption is further diverted towards the search for reusable, low cost, locally available, biodegradable adsorbents made from natural sources like fly ash[11,12], clay[13,14], peat[15], active sludge, rice husk, maize cob, starch, coconut shell, cotton[16], bajra powder[17] etc.