

REMOVAL OF CATIONIC DYES AND HEAVY METALS FROM WATER USING LOW COST ADSORBENTS

**Final Report of the Minor Research Project
[MRP (S)/13-14/KLMG031/UGC-SWRO dated 15-2-14]**

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CERTIFICATE



I hereby declare that, the Minor Research Project entitled “Removal of Cationic Dyes and Heavy metals from water using low cost adsorbents” (MRP (S)/13-14/KLMG031/UGC-SWRO dated 15-2-14) is a bonafide work carried out by Dr. Suma Bino Thomas, Associate professor, Department of Chemistry, Baselius College, Kottayam. Further certify that the work presented in the report is original and carried out according to the plan in the proposal and guidelines of the XII Plan of University Grants Commission.

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Kottayam, Kerala.

DECLARATION



I, Dr. Suma Bino Thomas hereby declare that the project work entitled “A study on experiences perceptions of capital market investors on financial derivatives” has been prepared by me and also declare that this is a bonafide record of research work done by me during the course of minor research project allotted to me by the University Grant Commission, New Delhi and no part of this study has been submitted earlier or elsewhere for any similar purpose.

Kottayam

Date: 24/05/2016

Dr. Suma Bino Thomas
(Principal Investigator)

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Chapter I
INTRODUCTION

Chapter I

INTRODUCTION

Environmental pollution due to industrial effluents is of major concern because of their toxicity and threat for human life and the environment. The discharge of textile effluents to the water bodies has raised much concern because of potential health hazards associated with the entry of toxic components into the food chains of humans and animals. Synthetic dyes are extensively used for dyeing and printing in a variety of industries. Over 10, 000 dyes with an annual production over 7×10^5 metric tons worldwide are commercially available and 5-10% of the dye stuff is lost in the industrial effluents.

Many industries, especially plating facilities and electronic manufacturing often lead to heavy metals containing in the effluent of waste water which is a serious environmental problems. All heavy metals are toxic and non-biodegradable and should be separated from waste water.

Synthetic dyes usually have a complex aromatic molecular structure such as benzene, naphthalene, anthracene, toluene, xylene, etc. The complex aromatic molecular structures of dyes make them more stable and difficult to biodegrade. Most of these dye wastes are toxic and may be carcinogenic. Many of these organic dyes are hazardous and may affect the aquatic life and even the food chain. Among the chemical classes of dyes, azo dyes are more versatile and account to more than half of the annual dye production. And also, azo dyes are considered more carcinogenic to humans.

Heavy metal contamination exists in aqueous waste streams of many industries such as metal purification, metal finishing, chemical manufacturing, mining operations, smelting, battery manufacturing, and electroplating. As a result of industrial activities and technological development, the amount of heavy metal ions discharged into streams and rivers by industrial and municipal wastewater have been increasing incessantly. Heavy metals are member of a loosely-defined subset of elements that exhibit metallic properties, which mainly includes the transition metals, some metalloids, lanthanides, and actinides.

Certain heavy metals such as iron, copper, zinc and manganese are required by humans for normal biological functioning. However, heavy metals such as mercury,

lead, cadmium are toxic to organisms. Most of the health disorders are linked with specific tendency of heavy metals to bio accumulate in living tissues and their disruptive integration into normal biochemical processes. Increased use of metals and chemicals in process industries has resulted in generation of large quantities of effluent that contains high level of toxic heavy metals and their presence poses environmental-disposal problems due to their non-degradable (2005).

Most heavy metals are cations, carrying a positive charge, such as zinc and cadmium. Soil particles tend to have a variety of charged sites on their surfaces, some positive while some negative. The negative charges of these soil particles tend to attract and bind the positively charged metal cations, preventing them from becoming soluble and dissolve in water. The soluble form of metals is more dangerous because it is easily transported, hence more readily available to plants and animals. Metal behavior in the aquatic environment is surprisingly similar to that outside a water body. Sediments at the bed of streams, lakes and rivers exhibit the same binding characteristics as soil particles mentioned earlier. Hence, many heavy metals tend to be sequestered at the bottom of water bodies. Yet, some of these heavy metals will dissolve. The aquatic environment is more susceptible to the harmful effects of heavy metal pollution. Metal ions in the environment bio accumulate and are biomagnified along the food chain. There, their toxic effect is more pronounced in animals at higher trophic levels.

Methods that are generally used such as chemical separation, filtration, membrane separation, electrochemical treatment ion exchange and exchange and adsorption. All these methods with the exception of adsorption are costly, have low output and are costly, have low output and are incapable of removing trace level of heavy metals from waste water. Adsorption has been shown to be a feasible alternative method for removing heavy metals from waste water.

Therefore there is a need to remove dyes and heavy metals before effluent is discharged into receiving water bodies. The most popular treatment methods for textile wastewater are combinations of biological treatment, chemical coagulation and activated carbon adsorption.

Cost is an important parameter for comparing the absorbent materials. Activated carbon has been recognized as a highly effective adsorbent for the treatment of heavy metals

in wastewater, but is readily soluble under extreme pH conditions. Activated carbon is most widely used adsorbent, as it has good capacity for adsorption of carcinogenic metals. However, high cost of activated carbon and 10-15% loss during the regeneration has determents in the utilization of activated carbon in the developing countries.

The cleaning of waste and waste water is one of most serious environmental problems of the present day. Discharge of dyeing industry wastewater into natural water bodies is not desirable as the colour prevents reoxygenation in receiving waters by cutting off penetration of sunlight. Dyes and pigments have been used in many industries for colouration purpose. Textile industry is one of the prominent polluters releasing high concentrated effluent into the surrounding environment. Dyes contain carcinogenic materials. Therefore, it is important to remove these pollutants. The removal of coloured and colourless organic pollutants is considered as an important application of adsorption processes.

There are a whole range of physical/chemical methods which have been effectively employed for colour removal, namely adsorption, membrane filtration, chemical oxidation, dissolved air floatation, coagulation/precipitation and electrochemical methods. Adsorption is the most effective and non-destructive technique that is widely used for the removal of dyes from aqueous solutions. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, use of operation and insensitivity to toxic substances. Adsorption has been used extensively in industrial process for separation and purification. The removal of coloured and colourless organic pollutants from industrial wastewater is considered as an important application of adsorption processes.

At present, there is a growing interest in using low cost, commercially available materials for the adsorption of dyes. A wide variety of materials such as potato peel, peat, various silicas, activated clay, banana pith, natural manganese mineral, shale oil ash, goat hair, alum sludge, natural zeolite, and mixtures of fly ash and soil have been investigated as low-cost alternatives to activated carbon. Many studies have been conducted to evaluate adsorption of dyes onto a wide range of natural and synthetic, organic and inorganic sorbents.

Adsorption techniques in colour removal

Adsorption has evolved into one of the most effective and feasible physical method for decolourisation of textile and dyeing wastewaters. The three different modes of contacting the adsorbent and waste water are as follows:

- 1) Batch contact
- 2) Fixed-bed contact and
- 3) Fluidized bed contact

Batch contact systems are highly effective on a smaller scale of operation, while the fixed-bed contact systems have the advantage of a constant dye concentration in contact with the adsorbent at all times. Though the fluidised-bed systems have high rate of mass transfer, the operating conditions are highly critical in terms of flow rates and loading volumes and hence call for careful control.

The various factors that influence the rate of adsorption in any system are as follows:

- 1) Dye concentration
- 2) Adsorbent particle size
- 3) Extent of agitation
- 4) Temperature
- 5) Adsorbent/solution ratio
- 6) pH of the solution and
- 7) equilibrium capacity of the adsorbent.

The most commonly used adsorbent for colour removal is activated carbon. Since activated carbon is relatively expensive, the emphasis has shifted towards low-cost adsorbents that can serve as viable alternative for activated carbon. The high cost of activated carbon, calls for regeneration for prolonged use, which again adds to the cost of the treatment process. The advantage of using low cost adsorbent is that, they can be used in a treatment process and then disposed off, without any associated costs of regeneration.

Objectives of the study:

The objectives of the study were as follows:

1. To evaluate the feasibility of using potato peel, pomegranate peel, egg shell, passion fruit peel, used black tea, sawdust, dried mango leaf, rice husk, ground nut shell and tamarind shell as low cost adsorbents.
2. To compare the adsorption of different dyes, namely methylene blue, malachite green, Eosin Yellow, Congo red and Crystal violet.
3. To compare the adsorption of different heavy metals namely Co, Cr, Ni & Cu
4. To study the effect of contact time, adsorbent dosage, temperature and concentration
5. To examine the applicability of Freundlich and Langmuir adsorption isotherms.
6. To examine the kinetic model of adsorption.

Chapter II

REVIEW OF LITERATURE

Many industries, such as dyestuffs, textile, paper and plastics, use dyes in order to colour their products and also consume substantial volumes of water. As a result, they generate a considerable amount of coloured wastewater. It is recognized that public perception of water quality is greatly influenced by the colour. Colour is the first contaminant to be recognized in wastewater. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable. Over 100,000 commercially available dyes exist and more than $7 \cdot 10^5$ tonnes per year are produced annually. Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater.

Due to increasingly stringent restrictions on the organic content of industrial effluents, it is necessary to eliminate dyes from wastewater before it is discharged. Many of these dyes are also toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms however, wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat and oxidizing agents.

Removal of heavy metals such as cadmium, lead, nickel, chromium and copper from aqueous solution is necessary because of the frequent appearance of these metals in waste streams from many industries, including electroplating, metal finishing, metallurgical, tannery, chemical manufacturing, mining and battery manufacturing. These problems has received considerable attention in recent years, primarily due to the concern that those heavy metals in waste streams can be readily adsorbed by marine animals and directly enter the human food chain, thus presenting a high health risk to consumers. Cadmium, for example, damages the kidneys; lead adversely affects red blood cells, the nervous system and the kidneys. Acute systemic poisoning can result from high exposure to hexavalent chromium. For environmental protection, waste solutions containing heavy metal elements need treatment systems that can remove these contaminants effectively.

During the past three decades, several physical, chemical and biological decolorization methods have been reported; few, however, have been accepted by the

paper and textile industries. Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of colouring materials. Most commercial systems currently use activated carbon as sorbent to remove dyes in wastewater because of its excellent adsorption ability. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies. However, although activated carbon is a preferred sorbent, its widespread use is restricted due to high cost. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents.

Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many non-conventional low-cost adsorbents, including natural materials, biosorbents, and waste materials from industry and agriculture, have been proposed by several workers. These materials could be used as sorbents for the removal of dyes from solution. Some of the reported sorbents include clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell), industrial waste products (waste carbon slurries, metal hydroxide sludge), biosorbents (chitosan, peat, biomass) and others (starch, cyclodextrin, cotton).

There are several reported methods for the removal of pollutants from effluents. The technologies can be divided into three categories: biological, chemical and physical. All of them have advantages and drawbacks. Because of the high cost and disposal problems, many of these conventional methods for treating dye wastewater have not been widely applied at large scale in the textile and paper industries.

2.1. Biological treatments

Biological treatment is often the most economical alternative when compared with other physical and chemical processes. Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants. However, their application is often restricted because of technical constraints. Biological treatment requires a large land

area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation. Biological treatment is incapable of obtaining satisfactory colour elimination with current conventional biodegradation processes. Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin. In particular, due to their xenobiotic nature, azo dyes are not totally degraded.

2.2 Chemical methods

Chemical methods include coagulation or flocculation combined with flotation and filtration, precipitation– flocculation with Fe(II)/Ca(OH)_2 , electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. These chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use. Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems.

2.3. Physical methods

Different physical methods are also widely used, such as membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis,) and adsorption techniques. The major disadvantage of the membrane processes is that they have a limited lifetime before membrane fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability. In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high-quality treated effluent. This process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application.

Adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances.

2.4. Adsorption using commercial activated carbons

Adsorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from waters, especially those that are practically unaffected by conventional biological wastewater treatments. However, amongst all the sorbent materials proposed, activated carbon is the most popular for the removal of pollutants from wastewater. Because of their great capacity to adsorb dyes, CAC are the most effective adsorbents. This capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to increase their properties. However, activated carbon presents several disadvantages. It is quite expensive, the higher the quality, the greater the cost, non-selective and ineffective against disperse and vat dyes. The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent. The use of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications. This has led many workers to search for more economic adsorbents.

2.5. Non-conventional low-cost adsorbents

Due to the problems mentioned above, research interest into the production of alternative sorbents to replace the costly activated carbon has intensified in recent years. Attention has focused on various natural solid supports, which are able to remove pollutants from contaminated water at low cost. Cost is actually an important parameter for comparing the adsorbent materials. According to Bailey et al., a sorbent can be considered low-cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry. Certain waste products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative sorbents. Many of them have been tested and proposed for dye removal.

The by-products from the agricultural and industrial industries could be assumed to be low-cost adsorbents since they are abundant in nature, inexpensive, require little processing and are effective materials. Plentiful agricultural and wood by-products may also offer an inexpensive and renewable additional source of activated carbon. These waste materials have little or no economic value and often present a disposal problem. The activated carbons prepared from by-products exhibited high sorption properties.

Another waste product from the timber industry is bark, a polyphenol-rich material. Bark is an abundant forest residue which has been found to be effective in removing dyes from water solutions. Because of its low cost and high availability, bark is very attractive as an adsorbent. Like sawdust, the cost of forest wastes is only associated with the transport cost from the storage place to the site where they will be utilized. Bark is an effective adsorbent because of its high tannin content. The polyhydroxy polyphenol groups of tannin are thought to be the active species in the adsorption process.

Because of their low cost and local availability, industrial solid wastes such as metal hydroxide sludge, fly ash and red mud are classified as low-cost materials and can be used as adsorbents for dye removal. Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Because of their low cost, abundance in most continents of the world, high sorption properties and potential for ion exchange, clay materials are strong candidates as adsorbents.

Clay materials possess a layered structure and are considered as host materials. They are classified by the differences in their layered structures. There are several classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pyrophyllite (talc), vermiculite and sepiolite. The adsorption capabilities result from a net negative charge on the structure of minerals. This negative charge gives clay the capability to adsorb positively charged species. Their sorption properties also come from their high surface area and high porosity. Montmorillonite clay has the largest surface area and the highest cation exchange capacity. Its current market price (about US\$ 0.04–0.12/kg) is considered to be 20 times cheaper than that of activated carbon.

Generally, a suitable non-conventional low-cost adsorbent for dye adsorption should meet several requirements: (i) efficient for removal of a wide variety of dyes; (ii) high capacity and rate of adsorption; (iii) high selectivity for different concentrations; and (iv) non-conventional adsorbents may have potential as readily available, inexpensive and effective sorbents. They also possess several other advantages that make them excellent materials for environmental purposes, such as high capacity and rate of adsorption, high selectivity for different concentrations, and also rapid kinetics (of dye from aqueous solutions). Chitosan has received considerable interest for dye removal due, to its excellent dye-binding capacities.

OTHER ADSORBENTS

1. FLY ASH

Gangoli *et al.* examined the suitability of fly ash as an adsorbent for the removal of heavy metal ions from the aqueous solutions. They concluded that metal ions might adsorb on fly ash because of its high content of silica and alumina. Two different fly ashes (Afsin-Elbistan and Seyitomer) are generally used the studies. Adsorption data were correlated using the linear forms of the Langmuir and Freundlich equations. The adsorption data fitted the Langmuir isotherm better since the correlation coefficients for the Langmuir isotherm were higher than those for the Freundlich equation. The Afsin-Elbistan fly ash with a high calcium content was found to be metal adsorbent as effective as activated carbon. Therefore there are good prospects for the adsorption of these metals on fly ash with high calcium content in practical applications in Turkey.

2. PEAT

Peat is a low grade carbonaceous fuel containing lignin, cellulose and humic acids as its major constituents, these bear polar functional groups such as alcohols, aldehydes, carboxylic acids, ketones and phenolic hydroxides which can all be involved in chemical bonding with the adsorbed pollutants. Peat has a polar character which tends itself to the adsorption of specific materials such as metals and polar organic molecules.

3. ZEOLITE

Zeolites are highly porous aluminosilicates with different cavity structures. Their structures consists of a three dimensional framework, having a negatively charged

lattice. The negative charge is balanced by cations which are exchangeable with certain cation in solutions. It is recognized that, like clay, their adsorption properties of zeolites result mainly from ion exchange capabilities.

4. EGG SHELL

Egg shell membrane is located on the inner surface of an egg shell. It is a dual membrane composed of fibers of polysaccharides collagen like proteins. The membrane demonstrates good adsorption characteristics due to the availability of sites containing substituting groups such as hydroxyl, amine and sulphonic groups with which reactive metals or dyes can react.

A comparison between the adsorption by activated carbon and egg shell membrane towards reactive levafix brilliant red E-4BA suggests that egg shell membrane has a higher capacity (80 mg g^{-1}) than the carbon (60 mg g^{-1}).

Generally, a suitable non-conventional low-cost adsorbent for dye adsorption should meet several requirements:

- (1) Efficient for removal of a wide variety of dyes.
- (2) High capacity and rate of adsorption.
- (3) High selectivity for different concentrations.

Non-conventional adsorbents may have potential as readily available, inexpensive and effective sorbents. They also possess several other advantages that make them excellent materials for environmental purposes, such as high capacity and rate of adsorption, high selectivity for different concentrations, and also rapid kinetics. Such a newly mined, low-cost material, egg shell, was used in this investigation as adsorbent for various heavy metals.

2.6. Adsorption Isotherms

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials.

Many studies have been conducted to evaluate adsorption of dyes onto a wide range of natural and synthetic, organic and inorganic sorbents. Highest adsorption capacities have been reported for: 940 mg Reactive Black 5, 1190 mg Reactive Orange

96 and 1750 mg Reactive Red 120/g cucurbituril; 104.2 mg Acid Green 27, 53,5 mg Acid Violet 27 and 51.0 mg Indigo Carmin/g living mycelium of *Trametes versicolor* ; 242 mg Basic Red 18/g palm-fruit; 13.95 and 15.17 mg Acid Blue 29/g peat and fly ash, respectively ; and 1119, 873, 875, 190 914, 312, 277, 158 and 250 mg Methylene Blue/g adsorbent for bark, rice husk, cotton waste, hair and coal, respectively ; 5.92 mg direct red and 4.42 mg acid brilliant blue/ g banana pith, respectively ; 159.0mg Maxilon Goldgelb GL EC 400 and 309.0 mg Maxilon Schwarz FBL-01 300/g granular activated carbon, and 14.9 mg Maxilon Goldgelb GL EC 400 and 55.86 mg Maxilon Schwarz FBL-01 300/g natural zeolite, respectively. 160 mg Drim yellow-K4G, 140 mg Drim blue-KBL and 100 mg Drim red K4BL/ g shale oil ash. Approximately 88% of Dianix Blue [125 mg/dm³] could be removed from wastewater with 75 mg/dm³ recycled alum sludge at pH 9.13; 97.9% of Levafix Brill Blue EBRA[1. g/dm³] could be removed with a solution containing minimum 3 g/dm³ by chemical precipitation at pH 10.5-11.0.

a) Freundlich Isotherm

The first mathematical fit to an isotherm was published by Freundlich and Küster (1894) and is a purely empirical formula for gaseous adsorbates,

$$x/m = kP^{1/n}$$

where x is the quantity adsorbed, m is the mass of the adsorbent, P is the pressure of adsorbate and k and n are empirical constants for each adsorbent-adsorbate pair at a given temperature. The function has an asymptotic maximum as pressure increases without bound. As the temperature increases, the constants k and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface. Taking log both sides of equation, we get,

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n} \log p$$

The equation above equation is comparable with equation of straight line, $y = mx + c$ where, m represents slope of the line and c represents intercept on y axis.

Plotting a graph between $\log(x/m)$ and $\log p$, we will get a straight line with value of slope equal to $1/n$ and $\log k$ as y -axis intercept.

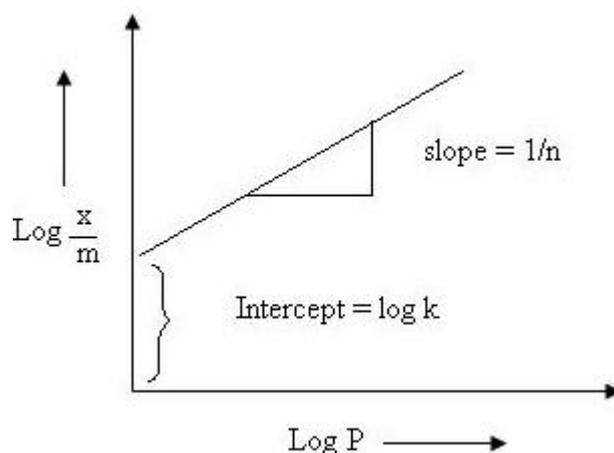


Fig.2.1. $\log(x/m)$ vs. $\log p$ graph

Limitation of Freundlich Adsorption Isotherm

Experimentally it was determined that extent of adsorption varies directly with pressure till saturation pressure P_s is reached. Beyond that point rate of adsorption saturates even after applying higher pressure. Thus Freundlich Adsorption Isotherm failed at higher pressure.

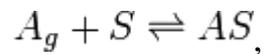
b) Langmuir Isotherm

In 1916, Irving Langmuir published a new model isotherm for gases adsorbed to solids, which retained his name. It is a semi-empirical isotherm derived from a proposed kinetic mechanism. It is based on four assumptions:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.
2. Adsorbed molecules do not interact.
3. All adsorption occurs through the same mechanism.
4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

These four assumptions are seldom all true: there are always imperfections on the surface, adsorbed molecules are not necessarily inert, and the mechanism is clearly not the same for the very first molecules to adsorb to a surface as for the last. The fourth condition is the most troublesome, as frequently more molecules will adsorb to the monolayer; this problem is addressed by the BET isotherm for relatively flat

(nonmicroporous) surfaces. The Langmuir isotherm is nonetheless the first choice for most models of adsorption, and has many applications in surface kinetics (usually called Langmuir-Hinshelwood kinetics) and thermodynamics. Langmuir suggested that adsorption takes place through this mechanism:



where A is a gas molecule and S is an adsorption site. The direct and inverse rate constants are k and k_{-1} . If we define surface coverage, θ , as the fraction of the adsorption sites occupied, in the equilibrium we have

$$K = \frac{k}{k_{-1}} = \frac{\theta}{(1 - \theta)P} \quad \text{or} \quad \theta = \frac{KP}{1 + KP}.$$

where P is the partial pressure of the gas or the molar concentration of the solution. For very low pressures $\theta \approx KP$ and for high pressures $\theta \approx 1$.

2.7. ADSORPTION REACTION MODELS

The study of sorption kinetics describes the adsorbate uptake rate and evidently this rate controls the residence time of adsorbate at the solid liquid interface. The different kinetic models, include the pseudo-first order, pseudo-second order, Elovich mass transfer, intraparticle diffusion, intraparticle diffusivity etc.

2.7.1. The Pseudo-First Order Equation

Lagergren (1898) presented a first-order rate equation to describe the kinetic process of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal, which is believed to be the earliest model pertaining to the adsorption rate based on the adsorption capacity. The pseudo-first order equation is generally expressed as:

$$dq_t/dt = k_1(q_e - q_t)$$

Where q_e and q_t are the sorption capacities at equilibrium and at time t , respectively (mg g^{-1}) and k_1 is the rate constant of pseudo-first order sorption (L min^{-1}). After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation becomes:

$$\text{Log}(q_e - q_t) = \text{log } q_e - k_1 t$$

When the values of $\text{log}(q_e - q_t)$ were linearly correlated with t , the plot of $\text{log}(q_e - q_t)$ versus t will give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the graph respectively.

2.7.2. The Pseudo- Second Order Equation

In 1995, Ho described a kinetic process of the adsorption of divalent metal ions onto peat in which the chemical bonding among divalent metal ions and polar functional groups on peat, such as aldehydes, ketones, acids, and phenolics are responsible for the cation-exchange capacity of the peat. The pseudo-second order chemisorption kinetic equation is expressed as eqn:

$$dq_t/dt = k_2 (q_e - q_t)^2$$

Where q_e and q_t are the sorption capacity at equilibrium and at time t , (mgg^{-1}) respectively and K_2 is the rate constant of the pseudo-second order sorption ($\text{g.mg}^{-1} \cdot \text{min}^{-1}$). For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of eqn becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t$$

Furthermore above eqn can be written as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$

If the pseudo-second order kinetics is applicable to the experimental data, the plot of t/q_t versus t of eqn (II) should give a linear relationship from which q_e , k and h can be determined from the slope and intercept of the plot respectively.

2.8. TYPES OF ADSORPTION

Adsorption can be classified into two categories as described below,

(1) Depending upon the concentration: In adsorption the concentration of one substance is different at the surface of the other substance as compared to adjoining bulk or interior phase.

(i) Positive adsorption : If the concentration of adsorbate is more on the surface as compared to its concentration in the bulk phase then it is called positive adsorption.

(ii) Negative adsorption : If the concentration of the adsorbate is less than its concentration in the bulk then it is called negative adsorption.

(2) Depending upon the nature of force existing between adsorbate molecule and adsorbent

(i) Physical adsorption: If the forces of attraction existing between adsorbate and adsorbent are Vander Waal's forces, the adsorption is called physical adsorption. This type of adsorption is also known as physisorption or Vander Waal's adsorption. It can be easily reversed by heating or decreasing the pressure.

(ii) Chemical adsorption: If the forces of attraction existing between adsorbate particles and adsorbent are almost of the same strength as chemical bonds, the adsorption is called chemical adsorption. This type of adsorption is also called as chemisorption or Langmuir adsorption. This type of adsorption cannot be easily reversed.

Comparison between physisorption and chemisorption

Physisorption (Vander Waal's adsorption)	Chemisorption (Langmuir adsorption)
Low heat of adsorption usually in range of 20-40kJ/mol	High heat of adsorption in the range of 50-400 kJ/mol
Force of attraction are Vander Waal's forces.	Forces of attraction are chemical bond forces.
It is reversible	It is irreversible
It is usually takes place at low temperature and decreases with increasing temperature.	It takes place at high temperature.
It is related to the case of liquefaction of the gas.	It is not related.
It forms multimolecular layers.	It forms monomolecular layers.
It does not require any activation energy.	It requires high activation energy.
High pressure is favourable. Decrease of pressure causes desorption	High pressure is favourable. Decrease of pressure does not cause desorption.

2.8.1. Factors which affect the extent of adsorption: The following are the factors which affect the adsorption,

(1) Nature of the adsorbate (gas) and adsorbent (solid)

(i) In general, easily liquefiable gases e.g., CO_2 , NH_3 , Cl_2 and SO_2 etc. are adsorbed to a greater extent than the elemental gases e.g. H_2 , O_2 , N_2 , He etc. (while chemisorption is specific in nature.)

(ii) Porous and finely powdered solid e.g. charcoal, fullers earth, adsorb more as compared to the hard non-porous materials. Due to this property powdered charcoal is used in gas masks.

(2) Surface area of the solid adsorbent

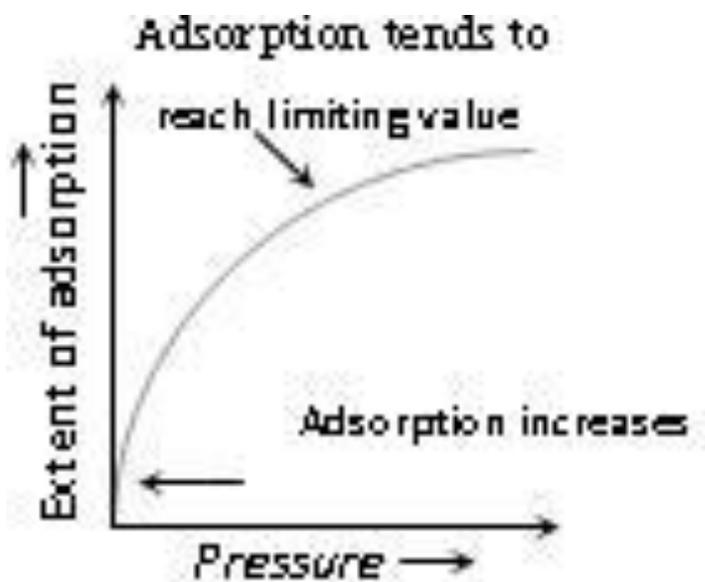
(i) The extent of adsorption depends directly upon the surface area of the adsorbent, i.e. larger the surface area of the adsorbent, greater is the extent of adsorption.

(ii) Surface area of a powdered solid adsorbent depends upon its particle size. Smaller the particle size, greater is its surface area.

(3) Effect of pressure on the adsorbate gas

(i) An increase in the pressure of the adsorbate gas increases the extent of adsorption.

(ii) At low temperature, the extent of adsorption increases rapidly with pressure.

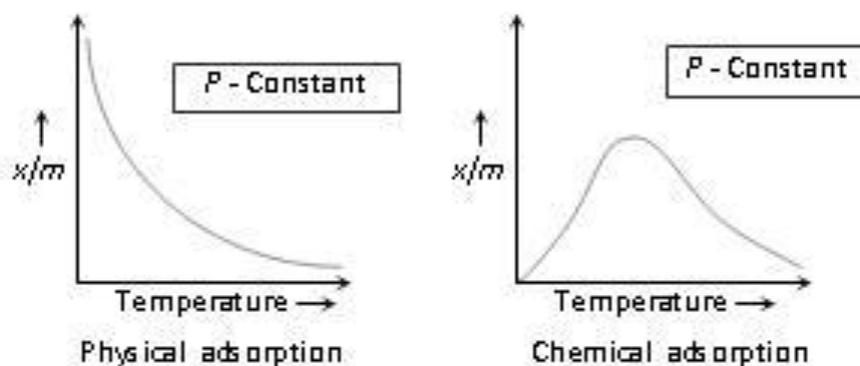


(iii) Small range of pressure, the extent of adsorption is found to be directly proportional to the pressure.

(iv) At high pressure (closer to the saturation vapour pressure of the gas), the adsorption tends to achieve a limiting value.

(4) Effect of temperature

(i) As adsorption is accompanied by evolution of heat, so according to the Le-Chatelier's principle, the magnitude of adsorption should decrease with rise in temperature.



(ii) The relationship between the extent of adsorption and temperature at any constant pressure is called adsorption isobar.

(iii) A physical adsorption isobar shows a decrease in x/m (where 'm' is the mass of the adsorbent and 'x' that of adsorbate) as the temperature rises.

(iv) The isobar of chemisorption shows an increase in the beginning and then decrease as the temperature rises.

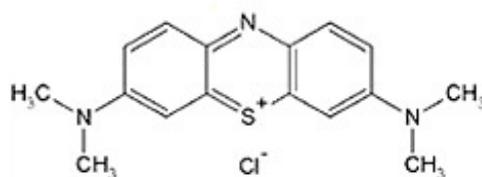
2.9. Dyes

The total dye consumption of the textile industry worldwide is more than 107 kg year⁻¹. There are more than 10,000 commercially available dyes with over 7×10^5 tones of dyestuff produced annually across the world. It is estimated that 2 % of dyes produced annually are discharged in effluent from manufacturing operations. While in the textile industry, it is estimated that 10–15% of the dye is lost during the dyeing process and released with the effluent. Effluents discharged from washing and dyeing processes represent 95% of the total amount of consumed water, namely 200 L per kg fabric. Synthetic dyes usually have a complex aromatic molecular structure such as benzene, naphthalene, anthracene, toluene, xylene, etc. The complex aromatic molecular structures of dyes make them more stable and difficult to biodegrade. Most of these dye wastes are toxic and may be carcinogenic. Many of these organic dyes are hazardous and may affect the aquatic life and even the food chain. Among the chemical classes of

dyes, azo dyes are more versatile and account to more than half of the annual dye production. And also, azo dyes are considered more carcinogenic to humans.

1. Methylene blue (MB)

Methylene blue is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$. It has many uses in a range of different fields, such as biology and chemistry. At room temperature it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water. The hydrated form has 3 molecules of water per molecule of methylene blue. Methylene blue should not be confused with methyl blue, another histology stain, new methylene blue, nor with the methyl violets often used as pH indicators. MB is the most commonly used material for dyeing cotton, wood, and silk with molecular weight 373.9 corresponds to methylene blue hydrochlorine with three groups of water. The structure of the methylene blue is given as below.



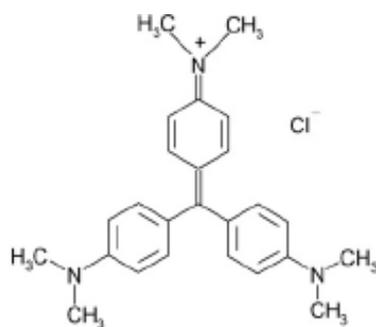
Recent research suggests that methylene blue, toluidine blue, and other 3,7-diaminophenothiazinium-based redox cyclers induce selective cancer cell apoptosis by NAD(P)H:quinone oxidoreductase (NQO1)-dependent bioreductive generation of cellular oxidative stress. Combined with plant auxin (indole-3-acetic acid), methylene blue is being investigated for the photodynamic treatment of cancer.

2. Crystal Violet

Crystal violet is also known under the name of gentian violet. It is a protein dye which stains the fatty portions of sebaceous sweat a deep purple color. Being a protein dye, crystal violet dye can also be used as an enhancer for bloody fingerprints. However, if this dye solution is going to be used on bloody prints, the first method shown here is recommended. Crystal violet dye is also used on most types of adhesive tapes, because conventional powders adhere to the entire sticky side of the tape and are not selective to the latent prints. It is a triarylmethane dye. The dye is used as a histological stain and

in Gram's method of classifying bacteria. Crystal violet has antibacterial, antifungal, and anthelmintic properties and was formerly important as a topical antiseptic. The medical use of the dye has been largely superseded by more modern drugs, although it is still listed by the World Health Organization.

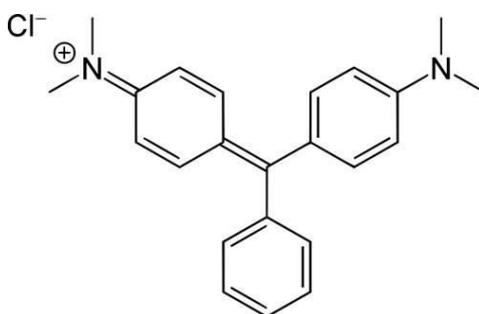
Crystal violet is not used as a textile dye. Instead it is used to dye paper and as a component of navy blue and black inks for printing, ball-point pens and ink-jet printers. It is also used to colourize diverse products such as fertilizers, anti-freezes, detergents, and leather jackets.



Crystal Violet

3. Malachite Green

Malachite Green (4-[(4-dimethyl amino phenyl) phenyl-methyl]-*N,N*-dimethyl aniline) Malachite green is an organic compound that is used as a dyestuff and has emerged as a controversial agent in aquaculture. Malachite green is traditionally used as a dye for materials such as silk, leather, and paper. Although called *malachite green*, the compound is not related to the mineral malachite — the name just comes from the similarity of colour.



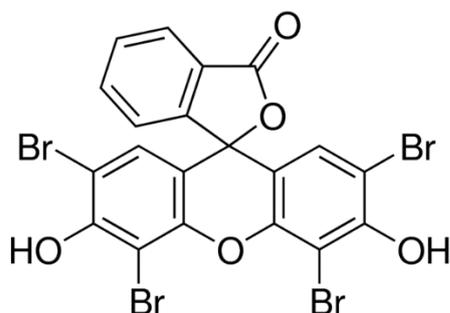
Malachite Green is classified in the dyestuff industry as a triarylmethane dye. Formally, Malachite Green refers to the chloride salt $[\text{C}_6\text{H}_5\text{C}(\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2)_2]\text{Cl}$, although the term Malachite Green is used loosely and often just refers to the coloured

cation. The oxalate salt is also marketed. The chloride and oxalate anions have no effect on the color. The intense green color of the cation results from a strong absorption band at 621 nm (extinction coefficient of $10^5 \text{ M}^{-1}\text{cm}^{-1}$). Malachite green is traditionally used as a dye. Millions of kilograms of MG and related triarylmethane dyes are produced annually for this purpose. Malachite green can also be used as a saturable absorber in dye lasers, or as a pH indicator between pH 0.2 - 1.8.

The LD₅₀ (oral, mouse) is 80 mg/kg. Rats fed malachite green experience “a dose-related increase in liver DNA adducts” along with lung adenomas. Leuco-malachite green causes an “increase in the number and severity of changes”. As leuco-malachite green is the primary metabolite of malachite green and is retained in fish muscle much longer, most intake of malachite green would be in the leuco form. During the experiment, rats were fed up to 543 ppm of leuco-malachite green, an extreme amount compared to the average 5 ppb discovered in fish. After a period of two years, an increase in lung adenomas in male rats was discovered but no incidences of liver tumors. Therefore it could be concluded that malachite green caused carcinogenic symptoms, but a direct link between malachite green and liver tumor was not established.

4. Eosin Yellow

Eosin is a water soluble dye, a red crystalline powder, designated by the formula $\text{C}_{20}\text{H}_8\text{O}_5\text{Br}_4$, used in textile dyeing and ink manufacturing or the red sodium salt of this powder, used in biology to stain cells, or any of a class of red acid dyes of the xanthene group used as cytoplasmic stains and as counter-stains.



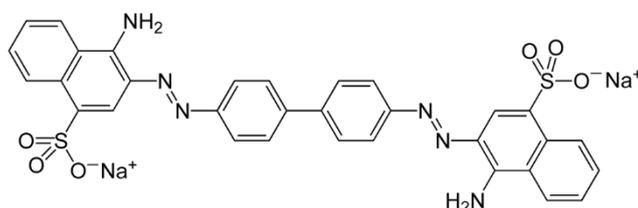
Eosin yellowish is a versatile red dye used in cosmetics, pharmaceuticals, textiles, etc., and as tissue stain, vital stain, and counterstain with hematoxylin. It is also used in special culture media.

The textile industry uses eosin for strong staining properties to efficiently dye nylon, silk, and wool. Additionally, the paper industry makes use of eosin as a ruling ink.

5. Congo red

Congo red is the sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(4-aminonaphthalene-1-sulfonic acid) (formula: $C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight: 696.66 g/mol). It is a secondary diazo dye. Congo red is water-soluble, yielding a red colloidal solution; its solubility is better in organic solvents such as ethanol. It has a strong, though apparently noncovalent, affinity to cellulose fibers. However, the use of Congo red in the cellulose industries (cotton textile, wood pulp, and paper) has long been abandoned, primarily because of its toxicity and tendency to run and change color when touched by sweaty fingers. The Congo red dye was first synthesized in 1883 by Paul Bottiger who was working then for the Friedrich Bayer Company in Elberfeld, Germany. Due to a color change from blue to red at pH 3.0-5.2, Congo red can be used as a pH indicator.

Due to a color change from blue to red at pH 3.0–5.2, Congo red can be used as a pH indicator. Since this color change is an approximate inverse of that of litmus, it can be used with litmus paper in a simple parlor trick: add a drop or two of Congo red to both an acid solution and a base solution. Dipping red litmus paper in the red solution will turn it blue, while dipping blue litmus paper in the blue solution will turn it red. This property gives Congo red a metachromatic property as a dye, both in strongly acidic solutions and with strongly acidophilic tissue.



Congo red has a propensity to aggregate in aqueous and organic solutions. The proposed mechanisms suggest hydrophobic interactions between the aromatic rings of the dye molecules, leading to a pi–pi stacking phenomenon. Although these aggregates

are present under various sizes and shapes, the "ribbon-like micelles" of a few molecules seem to be the predominant form (even if the "micelle" term is not totally appropriate here). This aggregation phenomenon is more prevalent in high Congo red concentrations, at high salinity and/or low pH.

In biochemistry and histology, Congo red is used to stain microscopic preparates, especially as a cytoplasm and erythrocyte stain. Apple-green birefringence of Congo red stained preparates under polarized light is indicative for the presence of amyloid fibrils. Additionally, Congo red is used in microbiological epidemiology to rapidly identify the presence of virulent serotype 2a *Shigella flexneri*, where the dye binds the bacterium's unique lipopolysaccharide structure.

2.10. Effects of heavy metals on human health

The heavy metals hazardous to humans include lead, mercury, cadmium, arsenic, copper, zinc, and chromium. Such metals are found naturally in the soil in trace amounts, which pose few problems. When concentrated in particular areas, however, they present a serious danger. Arsenic and cadmium, for instance, can cause cancer. Mercury can cause mutations and genetic damage, while copper, lead, and mercury can cause brain and bone damage. Next section presents the harmful effects to the three heavy metals that are prevalent in the environment.

1. Copper: Cu is heavily used in metal industries such as plating, mining and smelting, brass manufacture, electroplating industries, petroleum refining, and excessive use of Cu-based agrichemical mining (Demirbas *et al.*, 2008). About 98% of all Cu is used as metal, taking advantage of its distinctive physical properties by being malleable and ductile, a good conductor of both heat and electricity, and being resistant to corrosion. Cu is one of the relatively small groups of metallic elements which are essential to human health. Short periods of exposure can cause gastrointestinal disturbance, including nausea and vomiting. Long-term exposure to Cu can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea. Use of water that exceeds the Action Level over many years could cause liver or kidney damage.

2. Nickel: Electroplating is one important process involved in surface finishing and metal deposition for better life of articles and for decoration. Although several metals can be used for electroplating, nickel, copper, zinc and chromium are the most commonly used metals, the choice depending upon the specific requirement of the articles. During washing of the electroplating tanks, considerable amounts of the metal ions find their way into the effluent. Ni (II) is present in the effluents of silver refineries, electroplating, zinc base casting and storage battery industries (Sitting, 1976). Higher concentrations of nickel cause cancer of lungs, nose and bone. Dermatitis (Ni itch) is the most frequent effect of exposure to Ni, such as coins and jewelry. Acute poisoning of Ni (II) causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness.

3. Cobalt: As cobalt is widely dispersed in the environment humans may be exposed to it by breathing air, drinking water and eating food that contains cobalt. Skin contact with soil or water that contains cobalt may also enhance exposure. Cobalt is beneficial for humans because it is a part of vitamin B12, which is essential for human health. Cobalt is used to treat anaemia with pregnant women, because it stimulates the production of red blood cells. The total daily intake of cobalt is variable and may be as much as 1 mg, but almost all will pass through the body unadsorbed, except that in vitamin B12. However, too high concentrations of cobalt may damage human health.

4. Chromium: Chromium is used mainly in metal alloys such as metal-ceramics, stainless steel, and is used as chrome plating. It has high value in the industrial world because it can be polished to a mirror-like finish, and provides a durable, highly rust resistant coating, for heavy applications. On the flip side, chromium can also provide health benefits to humans.

Chromium is unstable in an oxygenated environment and, when exposed to air, immediately produces an oxide layer which is impermeable to further oxygen contamination. Chromium enters the environment through both natural processes and human activities. Increases in Chromium III are due to leather, textile, and steel

manufacturing; Chromium VI enters the environment through leather and textile manufacturing, but also due to industrial applications such as electro painting and chemical manufacturing. Groundwater contamination may occur due to seepage from chromate mines or improper disposal of mining tools and supplies, and improper disposal of industrial manufacturing equipment.

Chromium VI (hexavalent chromium) is considered carcinogenic only to animals in certain circumstances at this point; chromium in general is currently not classified as a carcinogen as the OSHA and is fairly unregulated, but is considered toxic, level 3. While chromium III is essential for regular operation of human vascular and metabolic systems as well as combating diabetes, too much chromium III may result in severe skin rash, or other more serious symptoms. Chromium VI is the most dangerous form of chromium and may cause health problems including: allergic reactions, skin rash, nose irritations and nosebleed, ulcers, weakened immune system, genetic material alteration, kidney and liver damage, and may even go as far as death of the individual.

2.11. Constituents of low cost adsorbents

1. POTATO PEEL: Potato peels are a potential source of dietary fiber. Potato peel is a nutrient rich waste and it contains adequate amount of nutrients such as carbohydrate and proteins. It also contains alcohol-insoluble solids (pectin, cellulose, starch), soluble sugars and minerals (mainly Ca, K, P, and Si). Potato peels are renewable, cheap and widely available waste. Utilization of waste potato peels to produce biomass appears to be economic. The biosorption ability of potato peels (as a new waste material obtained from commercial processing of potato chips factories) was investigated for removal of Pb(II), Cd(II) and Zn (II) from aqueous solutions. The percentage removals are 92, 75 and 42 % for Pb(II), Cd(II) and Zn(II), respectively at initial metal ion concentration of 100 mg/L and at room temperature.

2. POME GRANATE PEEL: The pomegranate, *Punica granatum* L., is an ancient, mystical, unique fruit borne on a small, long-living tree cultivated throughout the Mediterranean region, as far north as the Himalayas, in Southeast Asia, and in California and Arizona in the United States. In addition to its ancient historical uses, pomegranate

is used in several systems of medicine for a variety of ailments. The synergistic action of the pomegranate constituents appears to be superior to that of single constituents. In the past decade, numerous studies on the antioxidant, anti-carcinogenic, and anti-inflammatory properties of pomegranate constituents have been published, focusing on treatment and prevention of cancer, cardiovascular disease, diabetes, dental conditions, erectile dysfunction, bacterial infections and antibiotic resistance, and ultraviolet radiation-induced skin damage. Other potential applications include infant brain ischemia, male infertility, Alzheimer's disease, arthritis, and obesity.

The main constituents of Pomegranate peel are phenolic punicalagins, gallic acid and other fatty acids, catechin, quercetin, rutin, and other flavonols, flavones, flavonones and anthocyanidins.

3. PASSION FRUIT (*Passiflora edulis*) (Passifloraceae) : Passion fruit grows on a climbing vine that clings with tendrils and whose base lignifies with age. It can attain a length of several tens of metres. According to the variety, the plant grows in the tropics or in a warm, humid subtropical climate. Production starts 6 to 9 months after planting and continues on the same plant for 3 to 5 years. The nature of the plant means that it requires training for commercial production. Passion fruit is eaten fresh. Its exceptional fragrance makes it an essential tropical fruit. Its unattractive appearance and the problem of seeds slow its commercial development as a fresh fruit. In contrast, it is widely used in the agro food industry as juice (single or concentrate) and as a base for dairy products, ice cream etc. The passion fruit is round to oval, either yellow or dark purple at maturity, with a soft to firm, juicy interior filled with numerous seeds. The fruit is both eaten and juiced; passion fruit juice is often added to other fruit juices to enhance the aroma.

Fresh passion fruit is high in beta carotene, potassium, and dietary fibre. Passion fruit juice is a good source of ascorbic acid (vitamin C), and good for people who have high blood pressure. Some research is showing that purple passion fruit peel may help with controlling asthma symptoms. The fruit contains Lycopene in the mature and immature pericarp.

The rinds, which comprise much of this waste, could be used as an alternative raw material for extracting pectin. The most abundant component of pericarp was total dietary fibre (65%) and the exocarp fraction showed appreciable xylose content (123

mg per g). The highest content of pectin isolates (13.6%) of high esterification (79%) with highest viscosity (3.41 dl per g) was found in the mesocarp fraction, the lowest retention to the phenolic content of isolated pectin (15%) compared to the prepared flour prior to pectin extraction, and the HPSEC profile suggests the presence of a single population of polymers with high molar mass.

Chemical composition of passion fruit peel flour (g/100 g dry sample, except for moisture)

Moisture	9.93 ± 0.12
Ash	7.52 ± 0.02
Protein	4.05 ± 0.61
Lipid	Less than 0.10
Soluble fiber	19.20 ± 0.02
Insoluble fiber	38.05 ± 0.02
Carbohydrate	21.28 ± 0.44

4. USED BLACK TEA : In the present study a waste-material, used black tea (UBT), was apply as an adsorbent. Used black tea is an abundant and low cost natural adsorbent. The basic constituents which have a considerable influence on taste and color characteristics of tea include polyphenolic bodies, caffeine, non-caffeine nitrogenous compounds, pectic substances and minerals. Used black tea is renewable, cheap and widely available waste.

5. MANGO LEAVES : Mango is a fruit which is indigenous to the Indian subcontinent, belonging to the genus *Mangifera* and family Anacardiaceae. It is native to southern Asia, especially Burma and eastern India. Mango exists in two races, one from India and another from the Philippines and Southeast Asia. The Indian race is intolerant of excess moisture, has flushes of bright red new growth that are subject to mildew, bearing monoembryonic fruit of high color and regular form. The Philippine race, on the other hand, is able to tolerate humidity, has pale green or red new growth and resists mildew. Although there are various *Magnifera* species being grown many countries, the spesies *Magnifera indica*, also known as the Indian Mango or Common Mango, is the only mango tree commonly cultivated in many tropical and subtropical regions.

Mango trees are long-lived evergreen trees that grow 35–40 m tall, with a crown radius of 10 m. Mango fruits are popular with people around the world due to their sweet pleasant flavor and essential vitamins and dietary minerals provided such as vitamins A, B, B6, C, E and K. Mature mango leaves are dark green above and pale below; the leaves are orange-pink when they are young, rapidly changing to a dark gloss red. The midrib is pale and conspicuous and the many horizontal veins distinct.

Leaves of different trees are very versatile natured chemical species as these contain a variety of organic and inorganic compounds. Cellulose, hemicellulose, pectins and lignin present in the cell wall are the most important sorption sites. The important feature of these compounds is that they contain hydroxyl, carboxylic, carbonyl, amino and nitro groups which are important sites for metal sorption. Pineapple leaves, for instance, which are used in the study of Wenget *al.* for removal of methylene blue.

6. TAMARIND FRUIT SHELL: Tamarindus indica fruit shells (TIFSs) are naturally calcium rich compounds. The fluoride scavenging ability of TIFS carbons was due to naturally dispersed calcium compounds. Tamarind fruit shells have high ash content and fixed carbon and very less calorific value and volatile matter but it has long uniform fibrous lignocellulosic structure i.e they give good mechanical property but fails in combustion properties.

7. RICE HUSK: The total percentage composition of iron oxide ($\text{Fe}_2\text{O}_3 = 0.95\%$), Silicon dioxide ($\text{SiO}_2 = 67.30\%$) and Aluminum Oxide ($\text{Al}_2\text{O}_3 = 4.90\%$) was found to be 73.15%. Ye et al, reported physical properties of rice husk such as surface area of $438.05\text{m}^2/\text{g}$, bulk density of 0.3086 g/cm^3 and porosity of 0.38 by fraction. The chemical composition of rice husk by component analysis has been reported as 34.4% cellulose by weight, 29.3% hemicellulose by weight, 19.2% lignin by weight, 17.1% ash by weight, elemental analysis shows 49.3 % oxygen by weight, 44.6 % carbon by weight, and 5.6 % hydrogen by weight and by proximate analysis 59.5% volatiles by weight, 17.1 % ash by weight (composition of mineral ash $\text{SiO}_2, \text{K}_2\text{O}, \text{MgO}, \text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{CaO}$) and 7.9 % moisture by weight was found. As rice husk is insoluble in water, having good chemical stability, structural strength due to

high silica content so researchers are using it for treating heavy metal from ground water and surface water.

8. GROUND NUT SHELL: Groundnut botanically known as *Arachis hypogaea* belongs to Leguminosae family. Lignocellulosic fibers are constituted by three main components: hemicellulose, cellulose and lignin, which are known to present very complex structure. Cellulose, which is the main fraction of the fibers, is a semicrystalline polysaccharide made up of D-glucosidic bonds. A large amount of hydroxyl groups in cellulose gives hydrophilic properties to the natural fibers. Hemicellulose is strongly bound to the cellulose fibrils, presumably by hydrogen bonds. It consists of polysaccharides of comparatively low molecular weight built up from hexoses, pentoses and uronic acid residues. Lignin acts as the cementing agent in fiber, binding the cellulose fibers together. Chemical composition of groundnut shell is compared with the composition of selected species. The hemicellulose content of the fiber was found to be 18.7%, cellulose 35.7%, lignin 30.2% and Ash content 5.9%.

9. EGG SHELL: The chicken egg shell comprises calcified shell and shell membranes including inner and outer membranes. These membranes retain albumen and prevent penetration of bacteria. Shell membranes are also essential for the formation of eggshell. The organic matter of eggshell and shell membranes contain proteins as major constituents with small amounts of carbohydrates and lipids. Bronsch and Diamantstein (1965) analyzed uronic acid in eggshells and reported a significant correlation between the uronic acid content and the breaking strength of the shell. Uronic acid is a constituent sugar of glycosaminoglycan. We have shown that the organic matter of eggshell contains two glycosaminoglycans including hyaluronic acid and chondroitin sulfate-dermatansulfate copolymer. Sialic acid is another carbohydrate found in eggshell membranes. However, little is known about the difference in concentrations of sialic acid between the inner and outer eggshell membranes. There is also limited information available concerning variations in nitrogen concentrations and amino acid composition among the organic matter of eggshell and shell membranes. Eggshell and shell membranes are non-edible by-products with little saleable value. However, they may contain biologically active compounds.

10. USED BLACK TEA POWDER: The main constituents of tea leaves belong to the polyphenol group accounting for 25 to 35% on a dry weight basis. The polyphenols in tea mainly include the following six groups of compounds: flavanols, hydroxyl-4-flavanols, anthocyanins, flavones, flavonols and phenolic acids. Important and characteristic tea polyphenols are the flavanols of which catechins (flavan-3-ols) are pre-dominant and the major ones are: (-)-epicatechin (EC), (-)-epicatechin gallate (ECG), (-)epigallocatechin (EGC), (-)-epigallocatechin gallate (EGCG), (+)-catechin (C), and (+)-gallocatechin (GC). These compounds contribute to the bitterness, astringency and sweet aftertaste of tea beverages. Tea contains also favonols, mainly quercetin, kaempferol, myrecetin, and their glycosides. In black tea, the oxidation of polyphenols during processing leads to the formation of catechins and gallic acid complexes such as theaflavins, theaflavinic acids, thearubigins or theasinensis, and of proanthocyanidin polymers theobromine.

Tea contains many amino acids, but theanine, specific to the tea plant, is the most abundant, accounting for 50% of the total amino acids. Amino acid degradation is involved in the biogenesis of the tea aroma. Chlorophyll, carotenoids, lipids and volatile compounds are not major constituents in a tea brew but they also play an important role in the development of the aroma. Volatile fractions of tea leaves have been studied in detail and more than 600 different molecules have been isolated. These include terpenoids and degradation products of amino acids, carotenoids and linoleic acid. Tea also contains carbohydrates, vitamins E, K, A, low levels of B vitamins and vitamin C (in green tea only). Tea also provides useful amounts of potassium, manganese and fluoride ions to the diet.

Chapter III

EXPERIMENTAL

3.1. MATERIALS AND METHODS

Five different dyes namely Crystal violet, Methylene blue, Malachite green, Congo red and Eosin Yellow were obtained from Nice Chemicals, Kerala and Qualigen Fine Chemicals, Mumbai. The stock solution of these dyes was prepared in distilled water.

Four chemicals namely potassium dichromate, copper sulphate, cobalt nitrate and nickel sulphate were used in order to analyze the adsorption of Cr, Cu, Co and Ni respectively. The stock solutions of these metals were prepared in distilled water.

The adsorbents, Potato peel, Pome granate peel, Egg shell, Passion fruit peel, Saw dust, Mango leaves, Ground nut shell, Used black tea, Rice husk and Tamarind shell were collected and washed with distilled water. They were dried in sunlight, powdered and sieved. The adsorbents were characterized by IR spectroscopy and Scanning Electron Microscopy.

3.2. Batch experiments (Dye adsorption)

Dye adsorption experiments were performed by taking 50 ml stock solution of dye (500 mg /l). The variables studied were agitation time, adsorbent dose and concentration. After desired time of treatment samples were filtered to remove the adsorbent and progress of adsorption was determined spectrophotometrically using Photocolorimeter (Systronic) at the wavelength for maximum absorbance (λ_{\max}) which are 595nm, 661nm, 621 nm, 515-518nm and 497nm for crystal violet, methylene blue, malachite green, eosin yellow and congo red respectively. A blank was also carried out.

3.2. Batch experiments (Heavy Metal adsorption)

Adsorption experiments were conducted in which aliquots of dye solution with known concentrations were introduced into iodine flasks (250 cm³) containing accurately weighed amounts of the adsorbent. The bottles were shaken at room temperature using a shaker for a prescribed length of time to obtain equilibrium. The adsorbent was then removed by filtration. The equilibrium concentrations of metals

were determined by a Photocolorimeter (Systronic) at the wavelength for maximum absorbance (λ_{\max}) which are 590, 445, 500 and 540nm for Cu, Ni, Co and Cr respectively. A blank was also carried out.

3.2.1. Effect of adsorbent dose

The study was carried out with different dose of adsorbent of 400 μm average particle size ie; 0.5, 1.0, 1.5, 2.0 and 2.5 g. The concentrations of samples were 100mg/L and treated at room temperature for one hour.

3.2.2. Effect of agitation time

The experiments were carried out by taking 50 ml samples of dyes (concentration 100 mg/L) in separate flasks and treated with 0.05g of adsorbent dose at room temperature and was shaken well in an automatic shaker. The time period was varied from 10 min to 60minutes and after each 10min, adsorbent was removed by filtration and absorbance of the filtrate was measured.

3.2.3. Effect of concentration:

The samples were treated with constant dose of adsorbent (50mg) for one hour at room temperature. The concentrations of the adsorbate were 25, 50, 75, 100, 125 and 150 mg/L.

3.2.4. Adsorption Isotherm

Batch adsorption experiments were carried out in a shaker using 250ml-shaking flasks at room temperature for 60 min. The adsorbent (0.5 g) was thoroughly mixed with 50 mL of dyes solutions. The isotherm studies were performed by varying the initial dyes concentrations from 25 to 150 mg/L. After shaking the flasks for 60 min, the reaction mixture was analyzed for the residual dyes concentration.

3.2.5. Kinetics studies

Adsorption studies were conducted in 250-mL Iodine flasks and was thoroughly mixed individually with 50mL of dyes solution (100 and 125 mg/L) and the suspensions were shaken at room temperature. Samples were collected from the flasks at required time intervals viz. 10, 20, 30, 40, 50, and 60 min by filtration. The clear solutions were analyzed for residual dyes concentration in the solutions photometrically.

Chapter IV

RESULTS AND DISCUSSION

4.1. Potato peel as low cost adsorbent

Adsorption of dye, methylene blue (MB), malachite green (MG) and crystal violet (CV) which are cationic in nature, were studied on potato peel as a function of amount of adsorbent, agitation time and concentration of adsorbate.

4.1.1. IR-characterization of the adsorbent

In order to gain better insight into the surface functional groups available on the surface of the different investigated adsorbents, the IR spectra of adsorbent before and after adsorption of dye were recorded as shown in Figs. 4.1.1-4.1.4. Potato peel IR spectrum showed four intense bands, at 3332.1, 1737, 1645 and 1010.2 cm^{-1} . The band at 3332.1 cm^{-1} was attributed to the surface hydroxyl groups and chemisorbed water.

An examination of the adsorbent before and after sorption reaction possibly provides information regarding the surface a group that might have participated in the adsorption reaction and also indicates the surface sites on which adsorption has taken place.

Both spectra show the O-H stretching region at around 3300 cm^{-1} . However, a new band at 1584 cm^{-1} , which corresponds to the MG and MB and one at 1738 for CV confirms dye adsorption onto the potato peel. The maximum wavelengths (λ_{max}) and extinction coefficients (ϵ) of prepared dye solutions are given in Table 4.1. 1.

Table.4.1.1. Characterization of dyes

Dye	CAS No	Colour index No.	F.W. (gmol^{-1})	λ_{max} (nm)	ϵ ($\text{dm}^3/\text{mol. cm}$)
Methylene Blue	61-73-4	52015	319.85	661	73044
Malachite Green	569-64-2	42000	364.92	620	145603
Crystal Violet	548-62-9	42555	407.911	590	87000

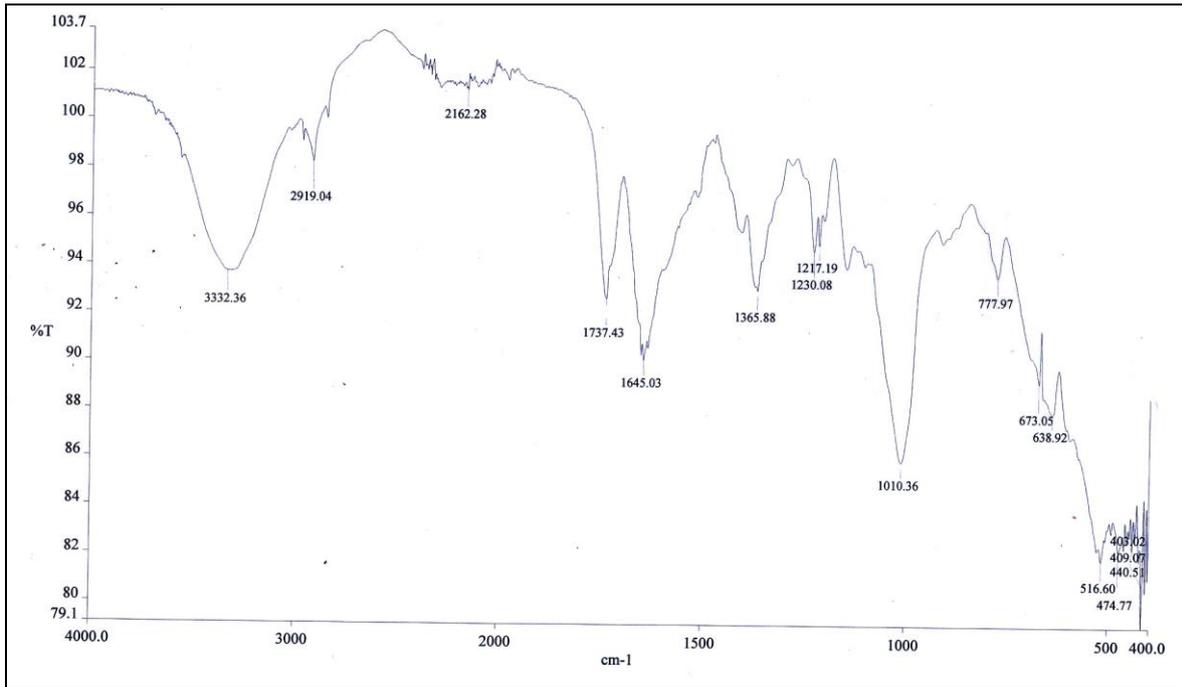


Fig.4.1.1. IR SPECTRUM OF POTATO PEEL

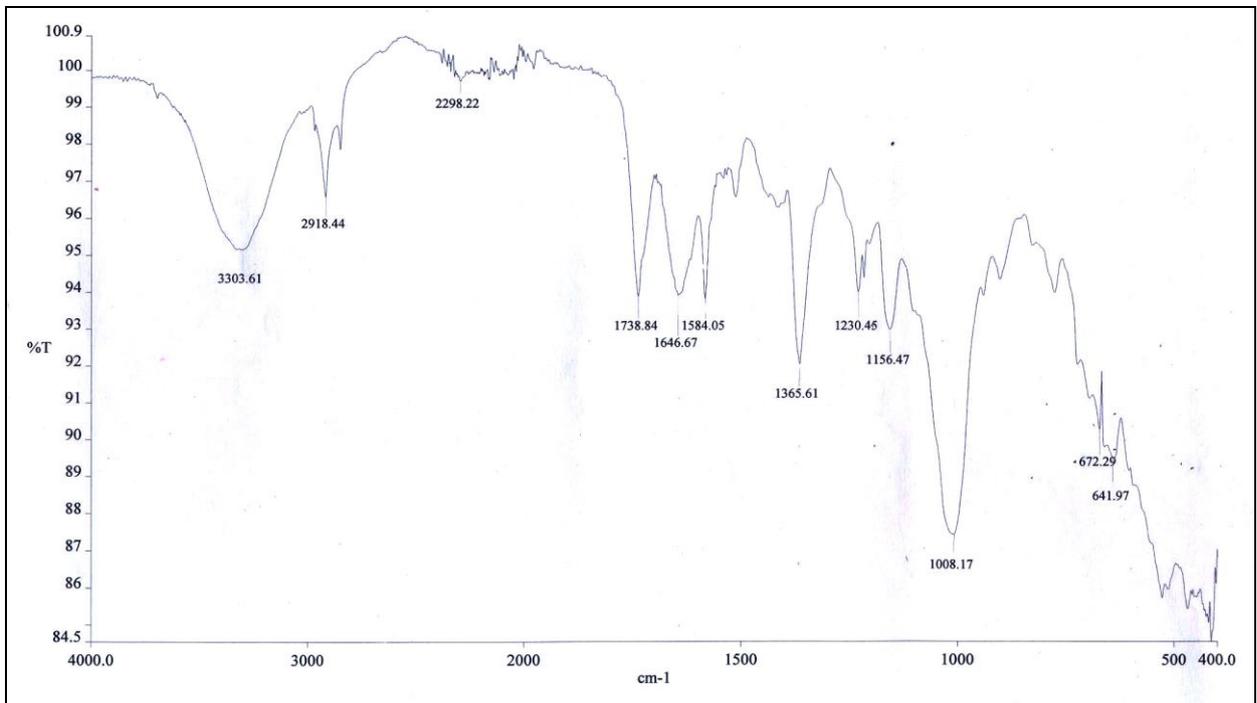


Fig. 4.1.2. IR SPECTRUM OF METHYLENE BLUE ADSORBED POTATO PEEL

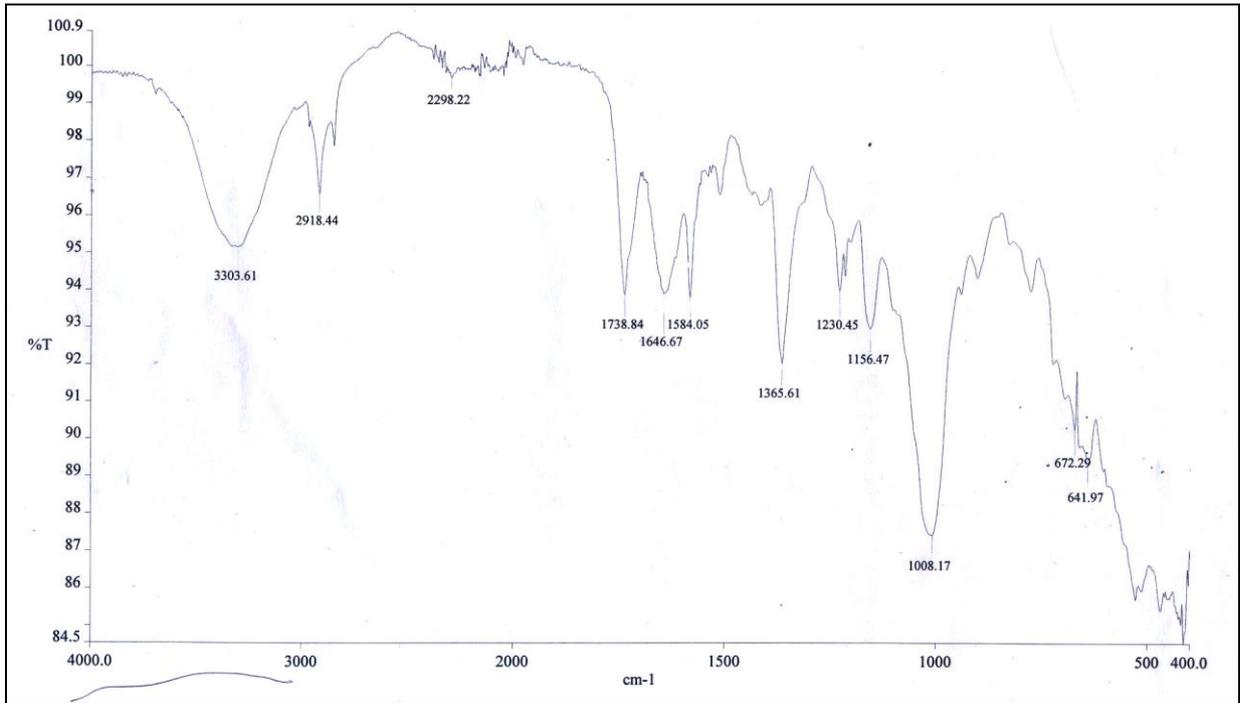


Fig. 4.1.3. IR SPECTRUM OF MALACHITE GREEN ADSORBED POTATO PEEL

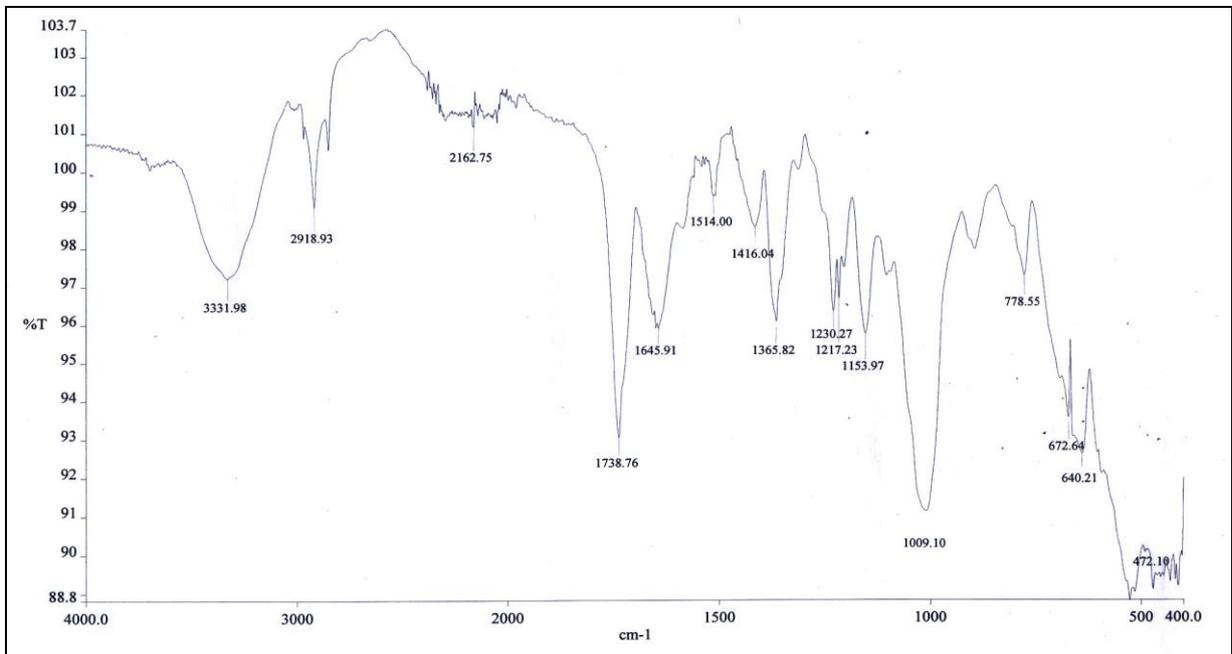
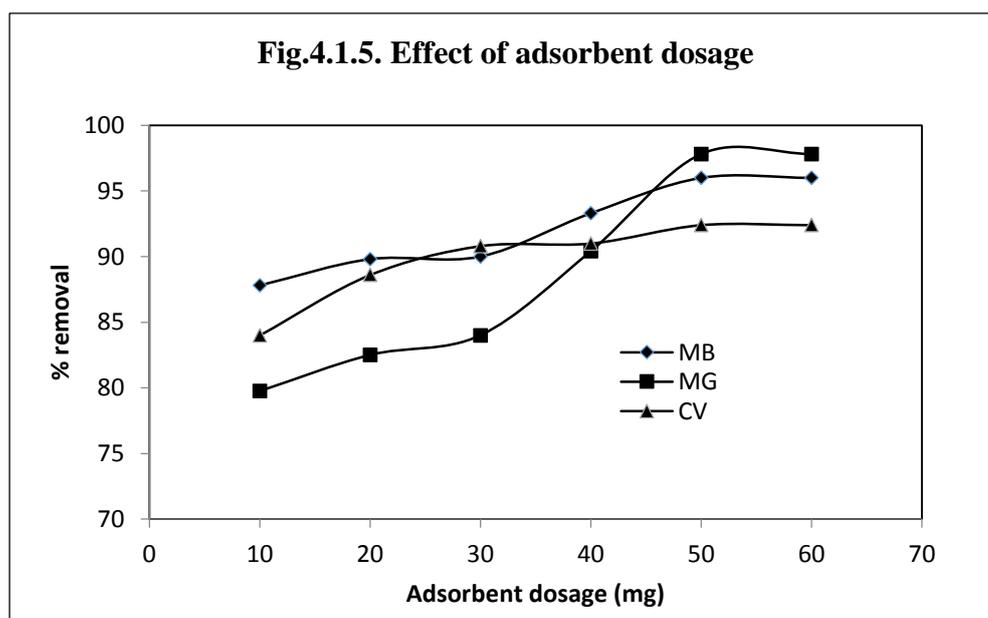


Fig 4.1.4. IR SPECTRUM OF CRYSTAL VIOLET ADSORBED POTATO PEEL

4.1.2. Effect of adsorbent dose

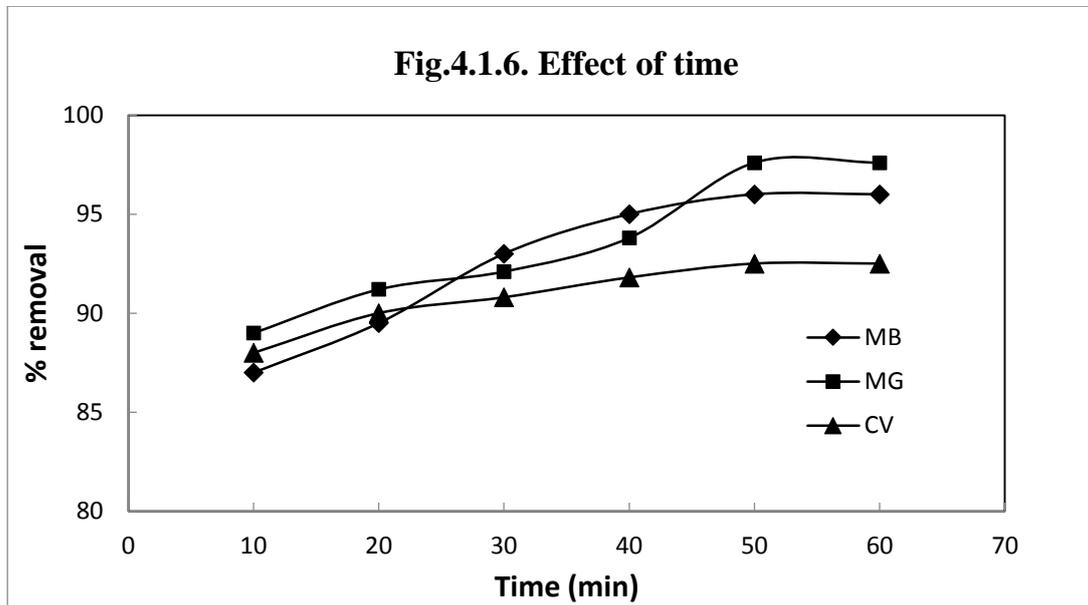
The effect of the adsorbent dose was studied at room temperature by varying the sorbent amounts from 10 to 60 mg. For all these runs, initial concentration of dyes were fixed as 100 mg/L. Figure 4.1.5. shows that adsorption of all the three dyes increases rapidly with increase in the amount of potato peel powder due to greater availability of the surface area at higher concentration of the adsorbent. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles. From the results, it is revealed that within a certain range of initial dye concentration, the percentage of dye adsorption on potato peel is determined by the sorption capacity of the powder. The maximum removal of dye was obtained in the adsorbent dose of 50 g/L.



4.1.3. Effect of contact time

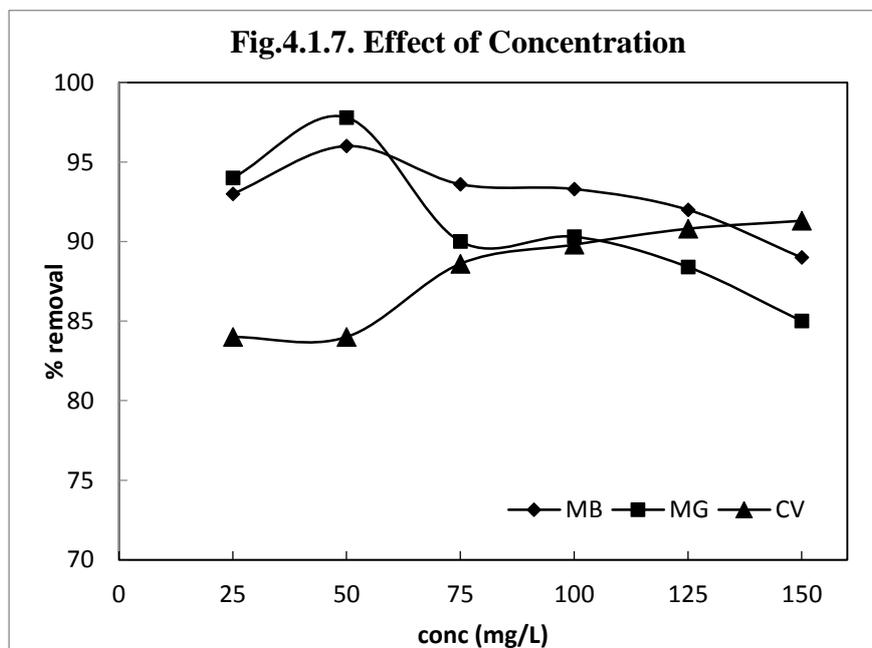
Adsorption of dyes was measured at different contact time for three different dyes. From Fig. 4.1.6, the plot reveals that the rate of percent of dye removal is higher at the beginning. This is probably due to larger surface area of the leaves being available at beginning for the adsorption of nickel ions. Most of the maximum percent nickel removal was attained after about 60 min of shaking time for different initial

concentrations. The increasing contact time increased the nickel adsorption and it remains constant after equilibrium reached in 50 min.



4.1.4. Effect of initial concentration

The effect of initial dye concentration in the range of 25 to 150mg/L on adsorption is shown in Fig. 4.1.7.



It is seen that the removal of dye was dependent on the concentration of dye as the increase in the initial concentration increased the amount of dye removed upto 50mg/L for methylene blue and malachite green and then the % removal decreased.

In the case of crystal violet it goes on increasing with the increase in initial concentration. The results indicate that potato peel adsorbs the largest quantity of malachite green followed by methylene blue and crystal violet respectively.

4.1.5. Isotherm data analysis

The parameters obtained from the different models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid-phase concentration was tested with the Langmuir and Freundlich isotherm equations.

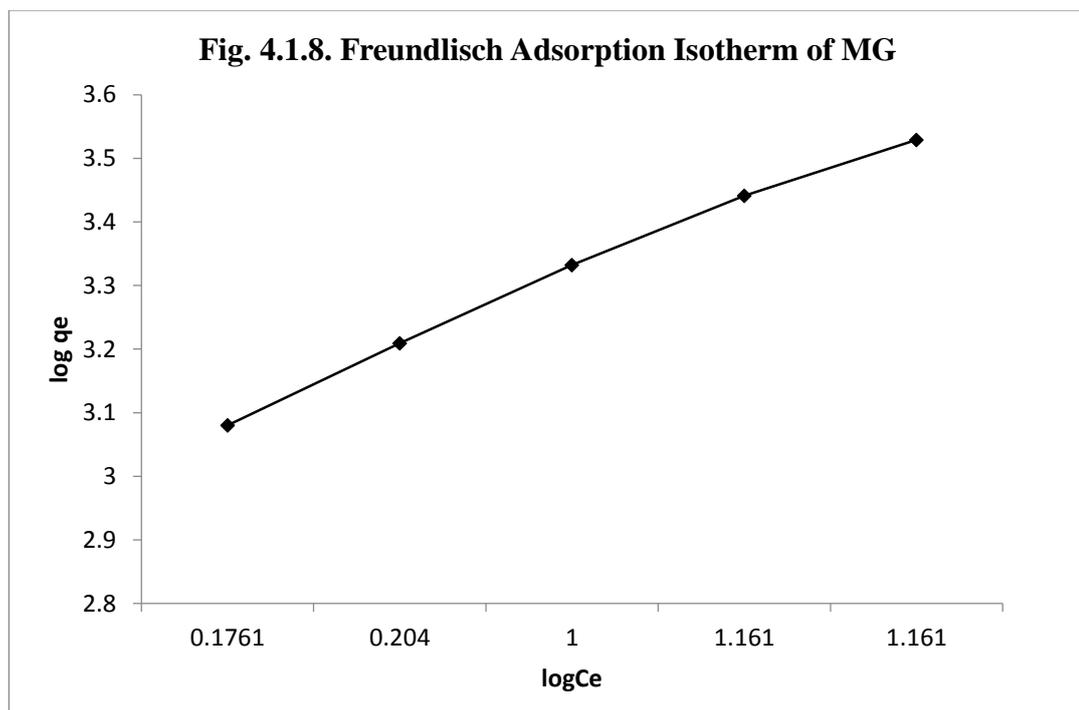


Fig. 4.1.9. Freundlich adsorption isotherm for crystal violet

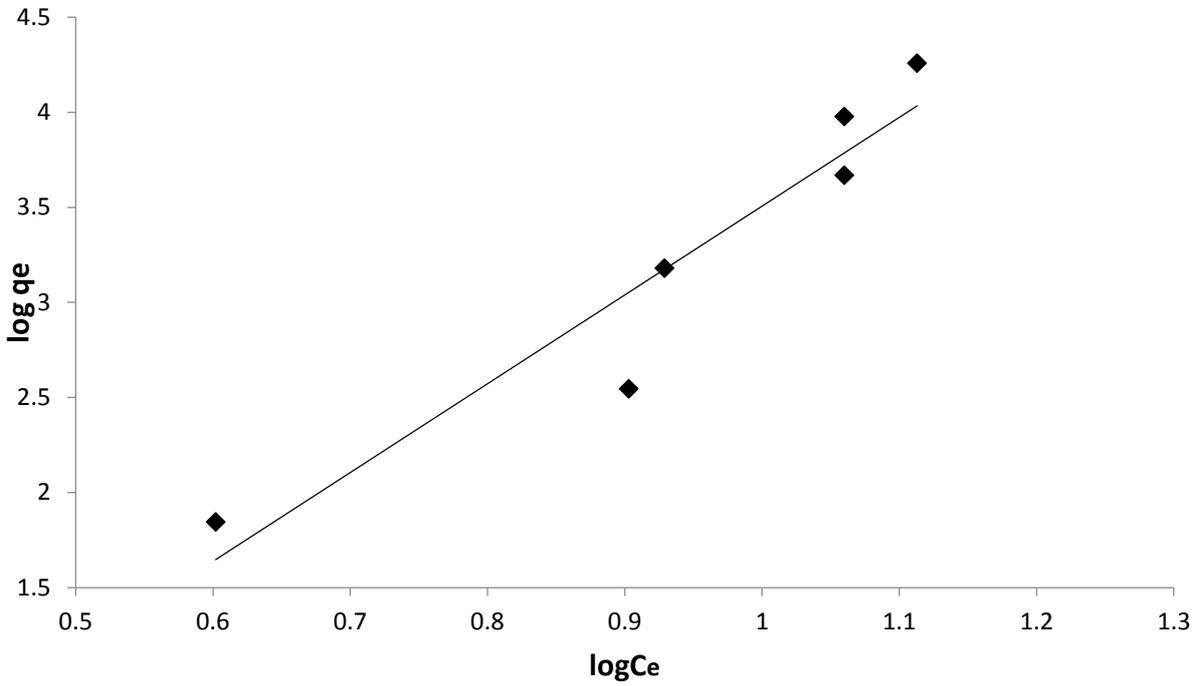
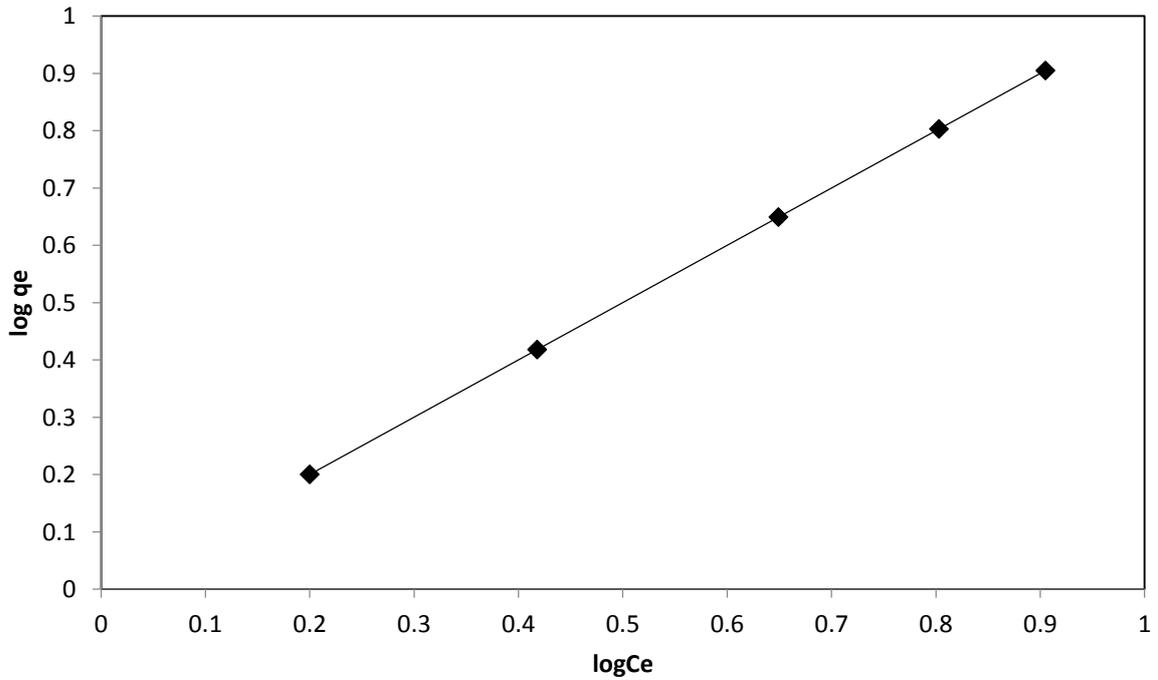


Fig.4.1.10.Freundlich Adsorption Isotherm of MB



The Freundlich isotherm models are shown in Fig.4.1.8-4.1.10. Freundlich adsorption isotherm model was found to be suitable for adsorption of methylene blue, crystal violet and malachite green on potato peel waste. The applicability of the linear form of Freundlich and Langmuir adsorption isotherm was proved by the high correlation coefficients $R^2 > 0.91$. Correlation coefficient for Freundlich is higher compared to that of Langmuir in all the three cases. But in the case of malachite green experimental results were fitted well with Langmuir and Freundlich isotherm models. Both the model confirmed a monolayer adsorption of dyes on orange peel waste.

Table.4.1.2. Kinetic parameters for Freundlich isotherm

Dyes	Statistical Parameter Constant		
	R^2	K	n
Malachite green	0.8996	1047.12	3.003
Methylene blue	0.9975	501.18	1.25
Crystal violet	0.9384	489.77	1.17

4.1.6. Kinetic models applied to the adsorption of dyes

The initial dye concentration of an effluent is important since a given mass of sorbent material can only adsorb a fixed amount of dye. The kinetics of dyes sorption was contact time dependent. Sorption increases with time and it remains constant after a contact time i.e. the equilibrium time. The response of the sorbent material used is not similar with all dyes used. The necessary time to reach equilibrium is in the range of 50min and, an increase of sorption time did not show notable effects. A possible explanation for the difference in sorption of the dyes can be given on the basis of their molecular weight and structural complexity. According Desai et al., the sorption kinetics and equilibrium are dependent upon the molecular dimensions of dyes.

For an appropriate description of the mechanism of dye sorption, it was necessary that different kinetic models be tested to determine their extent of fitness to the experimental sorption data. Thus, the kinetics of MB, MG and CV adsorption onto potato peel were analyzed using pseudo-first-order and pseudo second-order kinetic

models. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R^2 , values close or equal to 1). The relatively higher value is the more applicable model to the kinetics of dye adsorption onto potato peel.

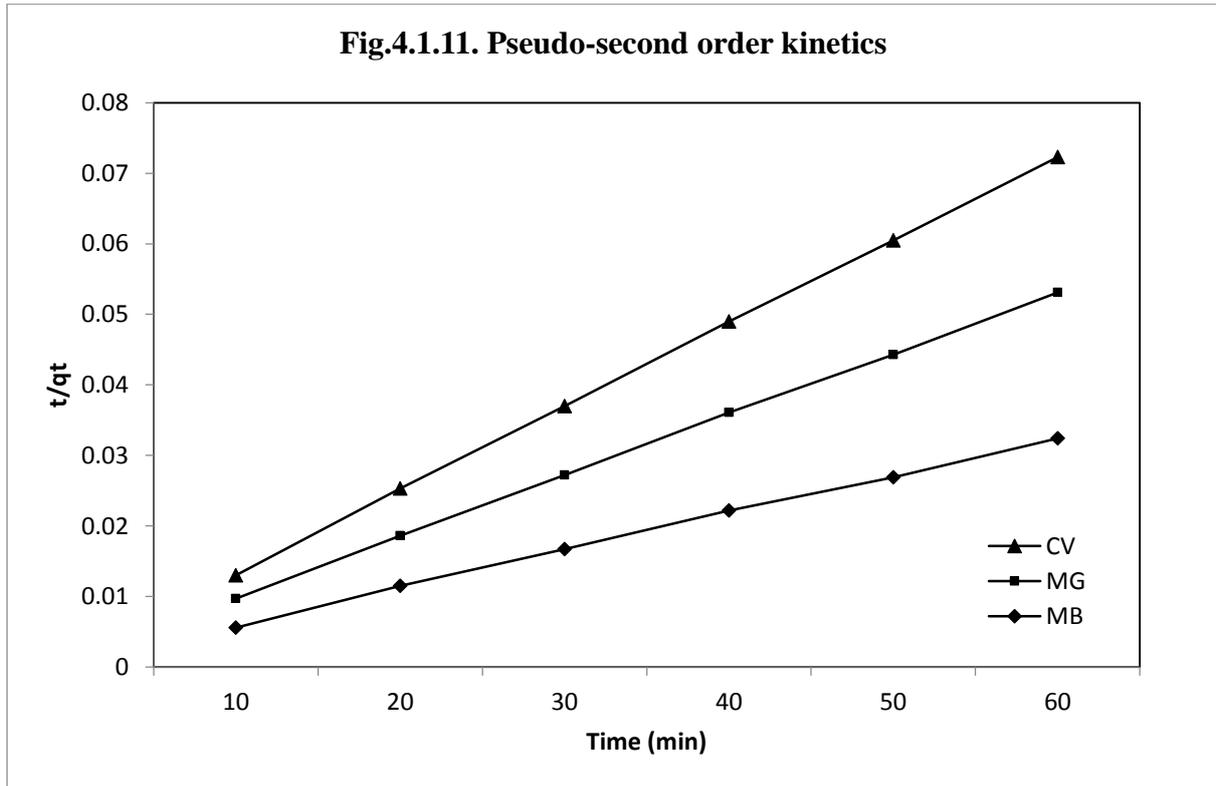


Table.3. presents the values of the linear coefficient of determination (R^2) values of the different kinetic models used to evaluate the sorption of dyes onto the potato peel. Examination of Table.4.1.3. shows that the pseudo-second order kinetic equation had the highest R^2 values. Thus this kinetic model was taken as the best fit equation for the description of the mechanism of sorption of dyes.

Table.4.1.3. The rate constant for Pseudo-second order adsorption

Dyes	K	q_e	R^2
Malachite green	2.90	4358.9	0.9991
Methylene Blue	3.479	1916	0.9963
Crystal violet	2.77	3333	0.9943

In addition, examination of the sorption capacity values (q_e) of the pseudo second order model shows that the values were in the same range as the experimental sorption capacity values. Therefore, the sorption of dyes from aqueous solution onto the potato peel waste adsorbents was found to follow the pseudo-second order kinetic equation. Furthermore, the pseudo-second order is based on the assumption that sorption follows a second order mechanism, with chemisorption as the rate limiting step. So the rate of occupation of adsorption sites is proportional to the square of number of unoccupied sites.

4.2. Pomegranate Peel as Low cost adsorbent

4.2.1. IR-characterisation of the adsorbent

In order to gain better insight into the surface functional groups available on the surface of the different investigated adsorbents, the IR spectra of adsorbent before and after adsorption of dye were recorded. The IR spectrum of pomegranate peel shows peaks at 3288.01, 2918.11 and 2849.67 cm^{-1} which refers to group (-OH), identical alkyl group(-CH₂-) and aldehyde group (-CHO), respectively. Also, the spectrum shows bands at 1717.77 and 1016.60 cm^{-1} were to be the presence of (C=C) and (C-O), respectively. The surface IR-characterization of pome granate peel indicated the presence of many functional groups which were able to bind with the cationic dyes. The band at 3288.01 cm^{-1} was attributed to the surface hydroxyl groups and chemisorbed water.

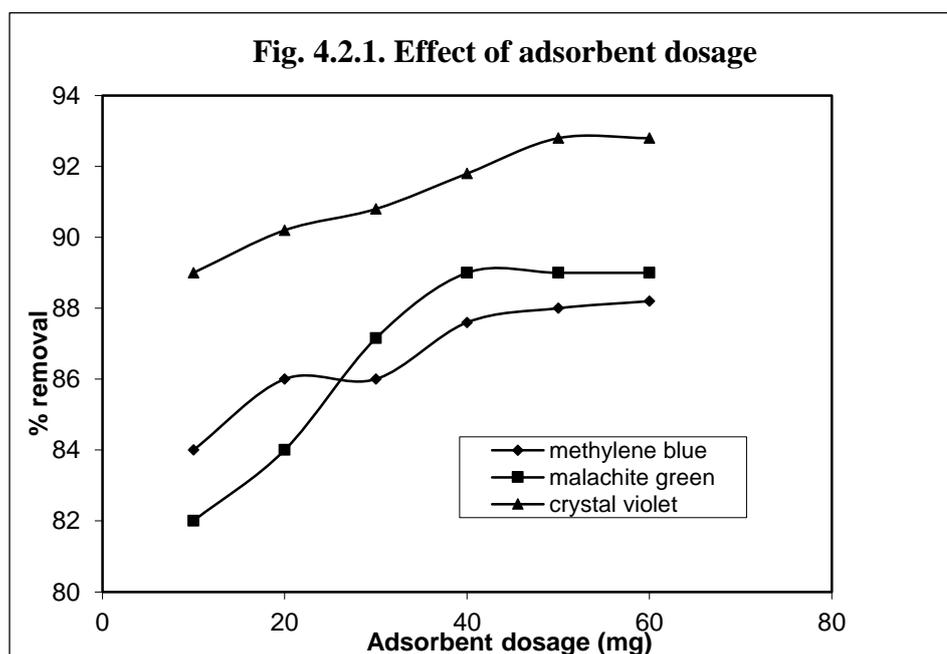
An examination of the adsorbent before and after sorption reaction possibly provides information regarding the surface a group that might have participated in the adsorption reaction and also indicates the surface sites on which adsorption has takes place. It was found that the spectra of treated sorbents did not differ significantly from the spectrum of the “parent” (untreated) material, suggesting that the treatment procedures did not change substantially the peel structure.

4.2.2. Effect of adsorbent dose

The effect of adsorbent dose was also investigated for the removal of dyes from aqueous solution. The experiments were carried out with adsorbent dose varied from 10 to 60 mg with keeping other parameters are constant. The removal of dyes was found to

be 82-89%, 84-88.2% and 89-92.8% in case of malachite green, methylene blue and crystal violet respectively (Figure.4.2.1.). The increase in removal of dyes with adsorbent dose is due to the introduction of more binding sites for adsorption.

The peel consists mainly of cellulose and lignin. Numerous hydroxyl groups in the molecules of these compounds represent main active sites for binding of ionic compounds, usually by an ion-exchange mechanism. However, some other binding mechanisms may occur on the peel sorbents, such as hydrogen bonding or hydrophobic interactions on the non-polar moieties of the peel matrix.

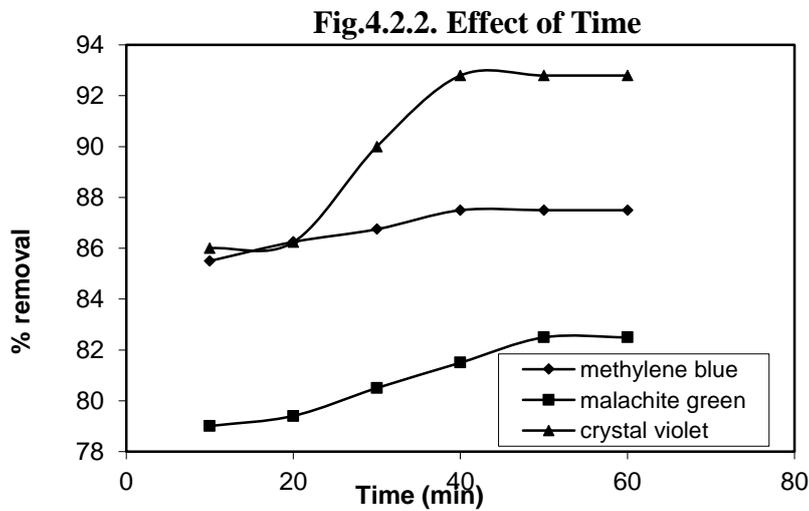


Peel is effective for removal of dye ions from water because of its high content of polyhydroxy polyphenolic groups that are capable of chelating dye ions. In addition, peel contains carboxylic groups, which can bind dye ions by ion-exchange mechanisms.

4.2.3. Effect of Shaking Time

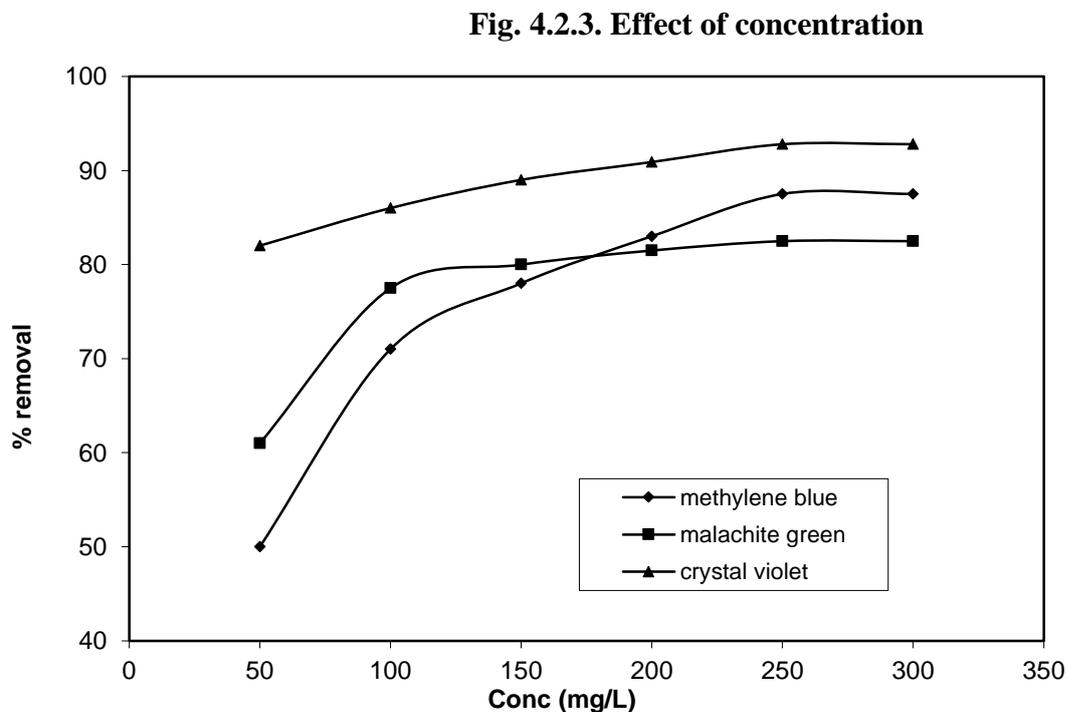
The time-dependent behaviour of dye adsorption was examined by varying the contact time between adsorbate and adsorbent in the range of 10-60 min. The concentrations of dyes were kept as 200mg/L while the amount of adsorbents added was 0.06 g. The dyes remaining plotted at a function of contact time (Figure. 4.2.2.) showed that the equilibrium between dyes and the adsorbents was attained within 40 min. Therefore, a 40 min shaking time was found to be appropriate for maximum adsorption and was used in all subsequent experiments. The removal of direct dyes by adsorption

increased with time and attained a maximum value in 40 min and thereafter it remained constant for all the concentrations studied.



4.2.4. Effect of initial concentration

The effect of concentration of dyes (50 to 300 mg/L) has been also tested with constant dose of adsorbent. The removal of dyes increased first from 83.5 to 87.5% in case of MB, 78.5 to 82.5 in case of CV and 85.75 to 92.8% in case of MG, reached a maximum value and remains constant(Fig.4.2.3). The results indicated that the adsorption of dyes is much dependent on concentration of solution.



4.2.5. Isotherm data analysis

The parameters obtained from the different isotherm models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. Langmuir and Freundlich isotherms are used for fitting the experimental data in adsorption studies to understand the extent and degree of favorability of adsorption. According to the obtained data for the model parameters it is obvious that Freundlich equilibrium model is favourable. Taking into consideration the values of the coefficient of correlation as criteria for goodness of fit, for most investigated Systems the Freundlich equation gives a better correlation between the theoretical and experimental data for the whole concentration range when compared with Langmuir equations.

The Freundlich constant, n also indicates the degree of favorability of adsorption. The Freundlich constant, n have values lying in the range of 1 to 10 for classification as *favorable* adsorption A smaller value of $(1/n)$ indicates a stronger bond between adsorbate and adsorbent while a higher value for k indicates rate of adsorbate removal is high. Hence it should be noted that the Isotherm constants are important in understanding the adsorption mechanism and their subsequent application for prediction of some important design parameters.

Table.4.2.1. Kinetic parameters for Freundlich isotherm

Dyes	Statistical Parameter Constant		
	R^2	K	n
Malachite green	0.8839	158.48	1.5
Methylene blue	0.9851	177.82	1.8
Crystal violet	0.9544	178.27	1.9

4.2.6. Kinetic models applied to the adsorption of MB, MG and CV

Several steps can be used to examine the controlling mechanism of adsorption process such as chemical reaction, diffusion control and mass transfer; kinetic models are used to test experimental data from the adsorption of MB, MG onto CV. The kinetics of dyes adsorption onto pome granate peel is required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes.

Thus, the kinetics of MB, MG and CV adsorption onto pome granate peel were analyzed using pseudo-first-order and pseudo second order kinetic models. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R^2 , values close or equal to 1). The relatively higher value is the more applicable model to the kinetics of dye adsorption onto pome granate peel.

Table.4. 2.2.The rate constant for Pseudo-second order adsorption

Dyes	K	q_e	R^2
Methylene Blue	3.57×10^{-5}	2000	0.9991
Malachite green	3.429×10^{-5}	1800	0.9963
Crystal violet	3.84×10^{-5}	5100	0.9943

4.3. Egg Shell as Low Cost Adsorbent.

4.3.1. Characterisation of the adsorbent

The IR spectral analysis is important to identify the characteristic functional groups on the surface of the adsorbent, which are responsible for adsorption of heavy metal ions. The IR spectrum of eggshell powder was recorded to obtain the information regarding the stretching and bending vibrations of the functional groups which are involved in the adsorption of the adsorbate molecules. The IR spectra of eggshell powder before and after fluoride adsorption are shown in Figure 4.3.1. The IR spectral analysis of eggshell powder shows distinct peak at 712.86, 875.56, 2516.00, 3431.25

cm.⁻¹The peak observed at 3431.25 and 2516.00 cm⁻¹ may be assigned to the presence of alcohol hydroxyl group (-OH) and acidic hydrogen group (-OH) stretching respectively. This result suggests that fluoride interacts with metal oxides and -OH functional group present in eggshell powder. The spectrum also shows some peaks positioned at 1648, 1528, 1308 and 1168 cm⁻¹. The bands at 1648 and 1528 cm⁻¹ reflect the carbonyl group stretching (amide) and N-H bending respectively. Bands at 1308.03 and 1168.70 cm⁻¹ correspond to C-H bending and C-O stretching respectively.

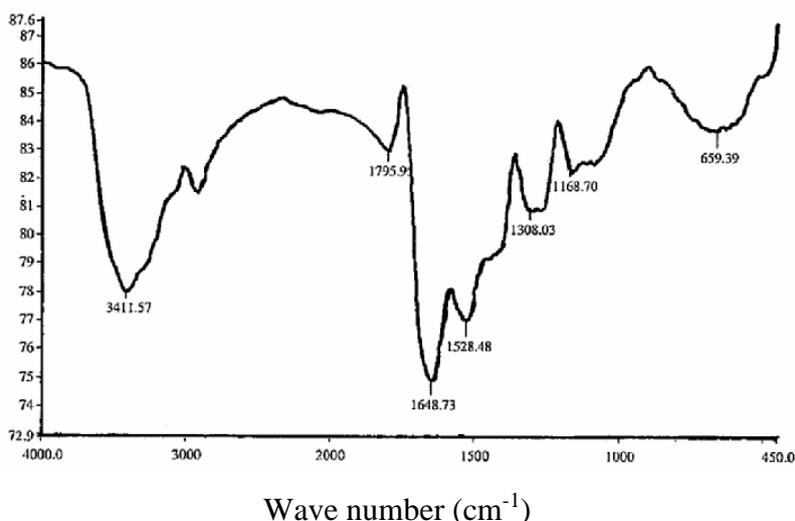


Fig.4.3.1. IR Spectrum of egg shell powder

SEM analysis is another useful tool for the analysis of the surface morphology of an adsorbent. The porous and irregular surface structure of the adsorbent can be clearly observed in SEM images shown in Figure 4.3.2.

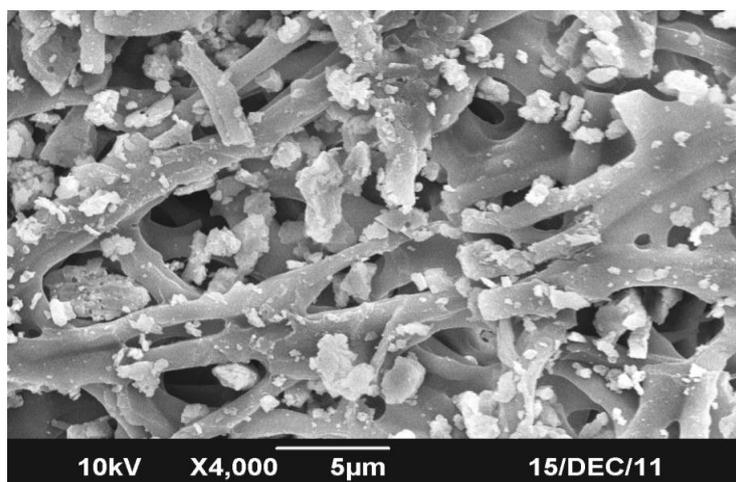
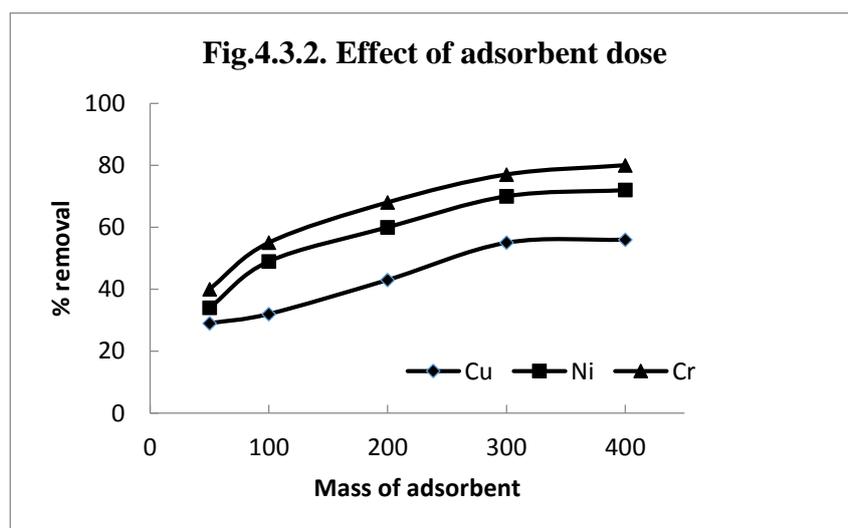


Fig.4.3.2. SEM of Egg shell powder

It clearly reveals the porous surface textures which endorse the adsorbent with increased surface area and high adsorption capacity. The heterogeneous pores and cavities provided a larger exposed surface area for the adsorption of metal ions.

4.3.2. EFFECT OF ADSORBENT DOSAGE

The effect of the adsorbent dose was studied at room temperature by varying the sorbent amounts from 50mg to 400mg. for all these runs, initial concentration of metal solution were fixed as 500mg/L. Fig.4.3.2. shows that adsorption of all the three metal ions increases as the amount of egg shell powder increases upto 300mg due to greater availability the surface area at higher concentration of the adsorbent. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. This may be due to the overlapping of adsorption sites as a result of overcrowding of adsorbent particles.

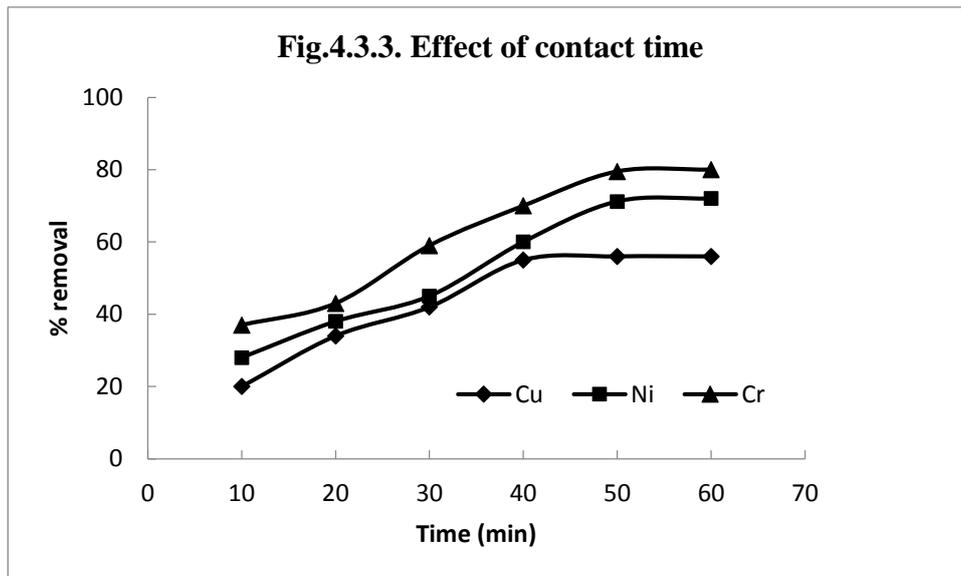


From the results, it is revealed that within a certain range of initial metal concentration, the percentage of metal adsorption on egg shell is determined by the sorption capacity of the powder. The maximum removal of metal was obtained in the adsorbent dose of 300mg.

4.3.3. EFFECT OF AGITATION TIME

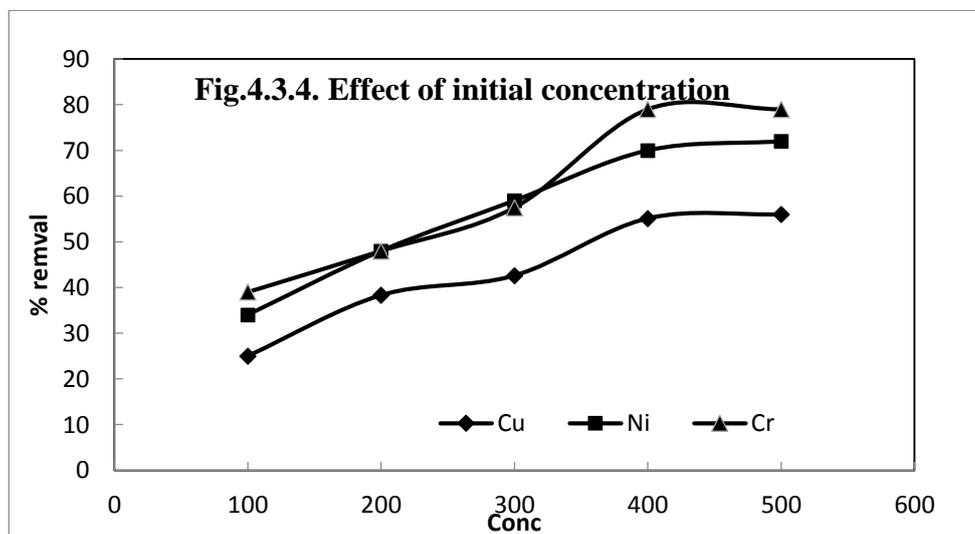
The samples of three metals were taken in separate flasks and treated with 0.3g of adsorbent. The variation in percent removal of dyes with the elapsed time has been shown in figure 4.3.3. It is evident from the figure that egg shell treatment resulted in 20% removal of copper in first 10minute, which increased up to 56% in 50 minutes. It

also shows that the percent removal of nickel and chromium are 45% and 38% in 10 minutes, which increased up to 72% and 80% in 40 minutes respectively for both the metals. The optimum time is 40 minutes for both the metals at which equilibrium is obtained. The increase in the extend of removal of metals with increasing time because adsorbate generally formed monolayer on the surface of adsorbent. Thus the removal of metals from aqueous solution is controlled by the rate of transport of the adsorbate species from the outer sites to the interior sites of adsorbent.



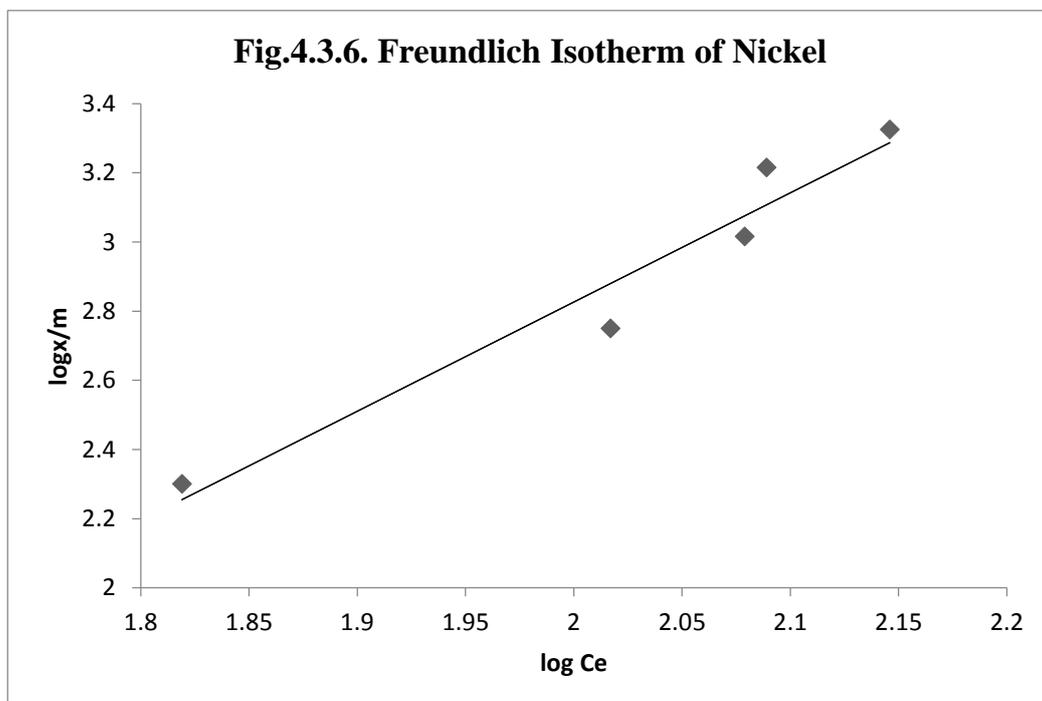
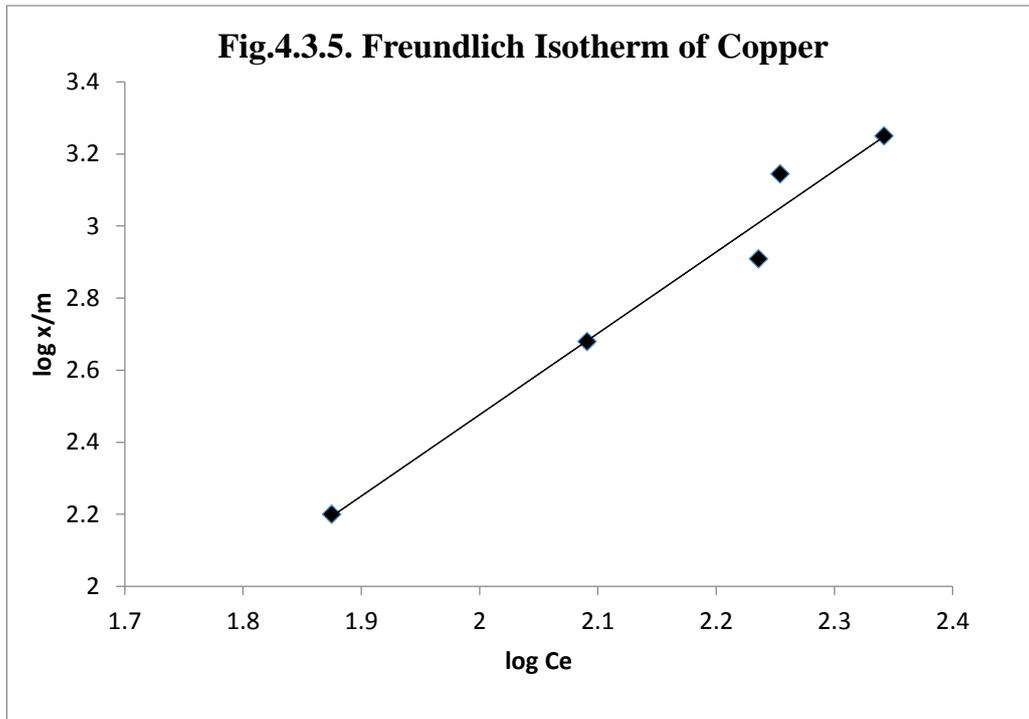
4.3.4. EFFECT OF INITIAL CONCENTRATION

The effects of concentration of metals 100 to 500ppm have been also tested with constant dose of adsorbent.



The removal of metals increased from 15 to 43% in case copper. 22 to 48% in case of nickel and 35 to 61% in case of chromium. The results indicated that the adsorptions of metals are much dependent on concentration of solution.

4.3.5. Isotherm data analysis



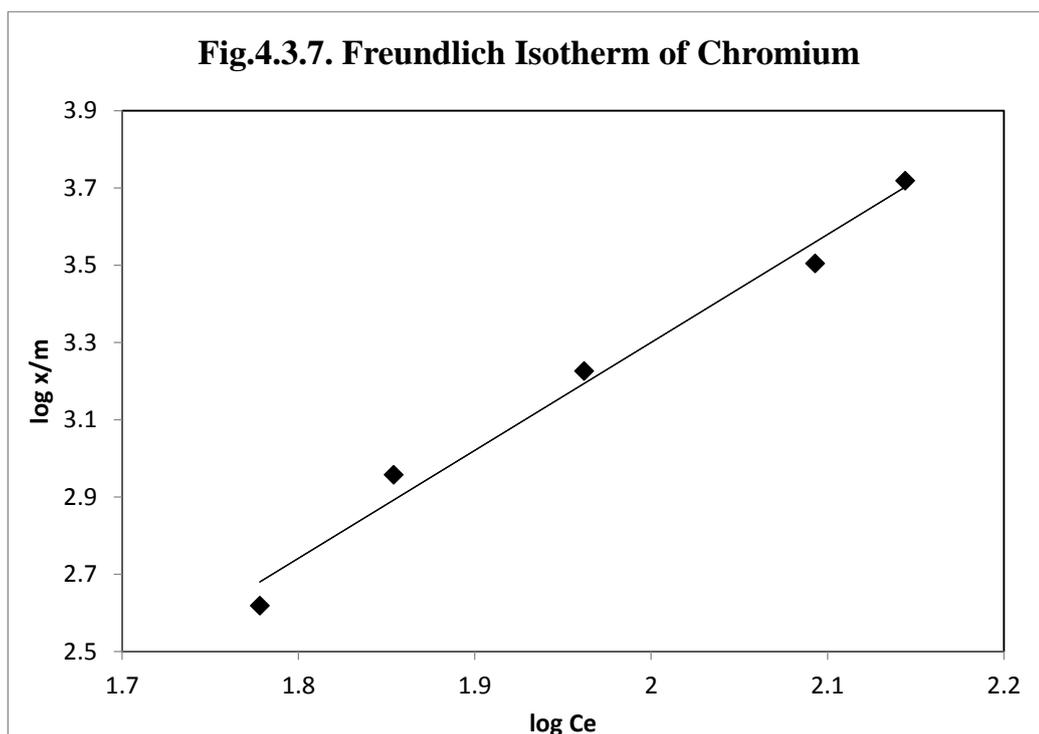
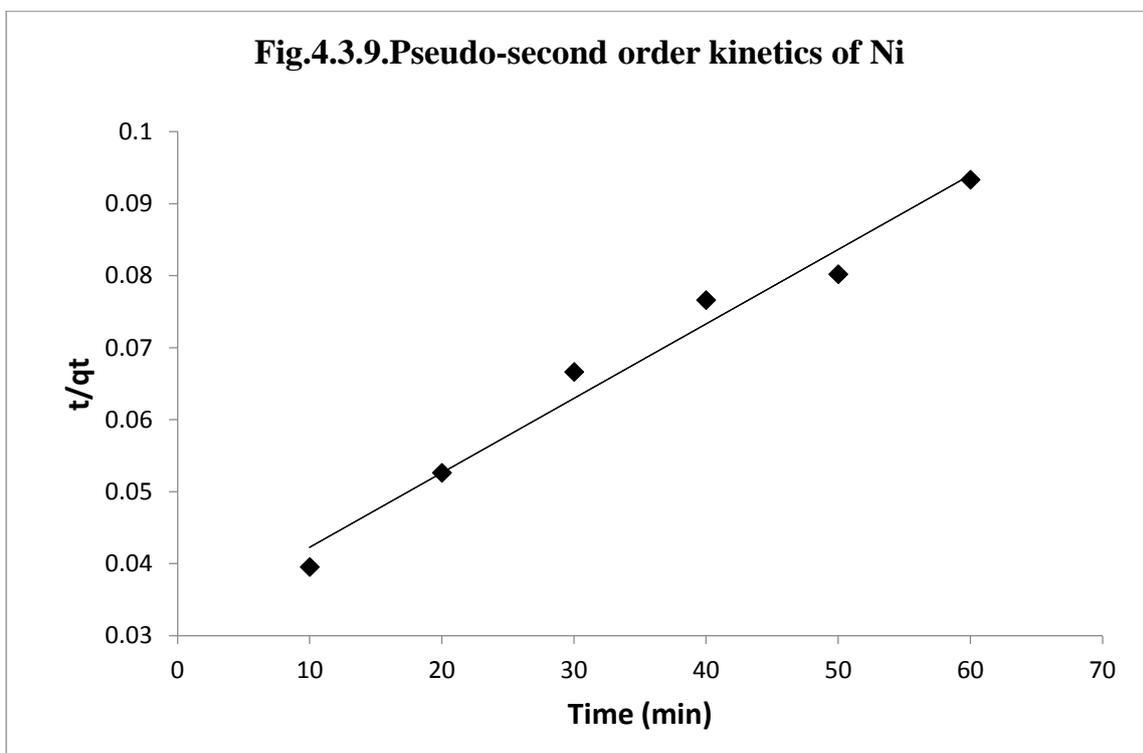
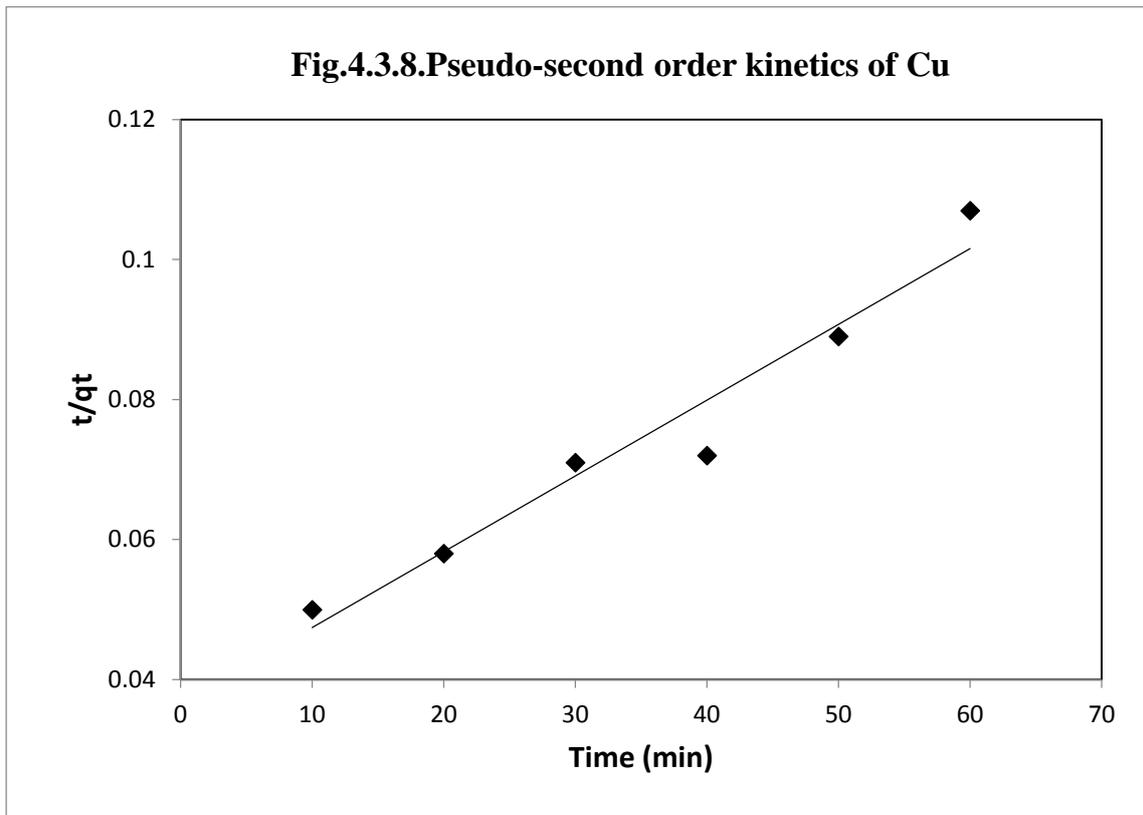


Table. 4.3.1. Kinetic parameters for Freundlich Isotherm

Metals	Statistical parameter constants			
	r	R²	K	n
Copper	0.9942	0.9862	9.1201×10^{-3}	0.4428
Nickel	0.9522	0.9732	3.258×10^{-4}	0.3168
Chromium	0.9920	0.9918	9.200×10^{-3}	0.4480

The parameters obtained from the different isotherm model provide important information on the adsorption mechanisms & surface properties and affinities of the adsorbent. According to the obtained data for the model parameters it is obvious that Freundlich equilibrium model is favorable. The Freundlich constant, n also indicates the degree of favorability of adsorption. The Freundlich constant, n has values lying in the range of 1 to 10 for classification as favorable adsorption.

4.3.6. Kinetic models applied to the adsorption of metals



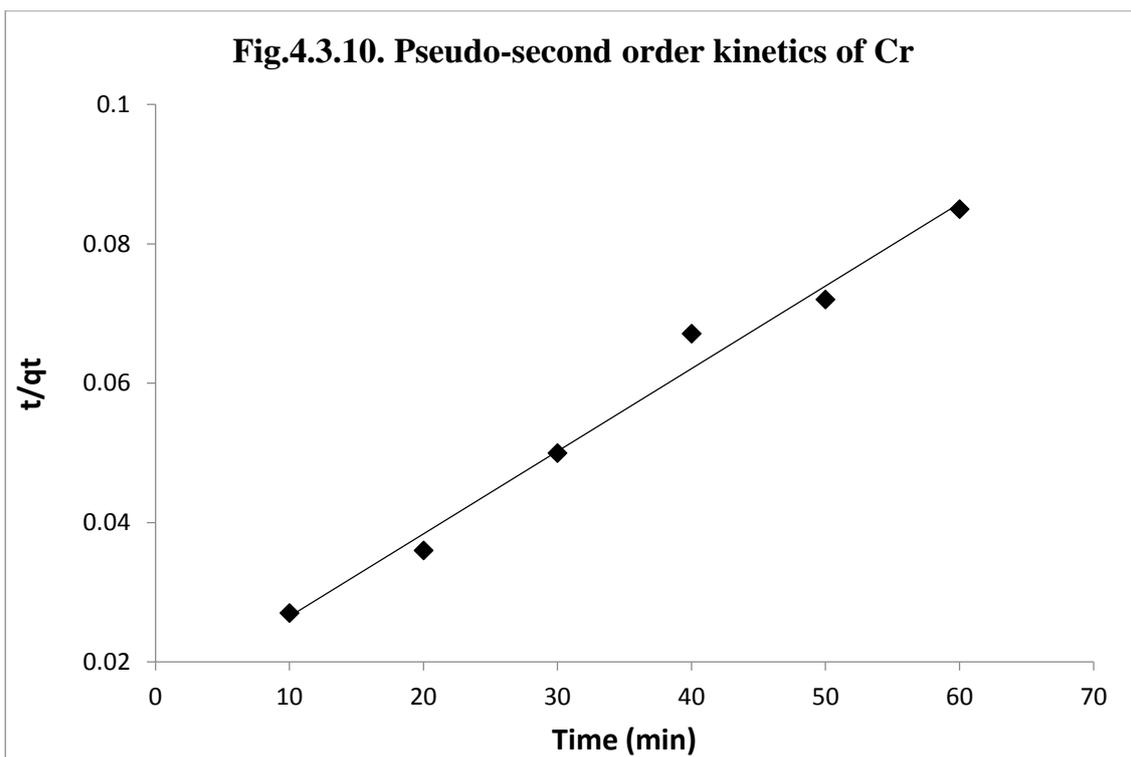


Table.4.3.2. Pseudo-second order parameters

Metals	Statistical parameter constants			
	r	R ²	q _e	k _{ad} (x10 ⁻⁵)
Copper	0.9752	0.9510	900.00	2.77
Nickel	0.9883	0.9760	970.87	3.325
Chromium	0.9928	0.9850	1143.17	9.588

The kinetics of Cu, Ni and Cr adsorption onto egg shell powder were analyzed using pseudo-first-order and pseudo second order kinetic models. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R², values close or equal to 1). The relatively higher value is the more applicable model to the kinetics of dye adsorption onto egg shell powder.

4.4. Passion Fruit Peel as Low Cost Adsorbent

4.4.1. Characterisation of the adsorbent

In order to gain better insight into the surface functional groups available on the surface of the different investigated adsorbents, the IR spectra of adsorbent before and after adsorption of dye were recorded as shown in Figs.4. 1-4. The IR spectrum of

passion fruit peel shows peaks at 3319.21 and 2918.09 cm^{-1} which refers to (-OH) and identical alkyl group(-CH₂-) respectively.

Fig.4.4.1. IR Spectrum of passion fruit peel



Also, the spectrum shows bands at 1736.71 and 1013.07 cm^{-1} were to be the presence of (C-O) and (-OH), respectively. The band at 3319.21 cm^{-1} was attributed to the surface hydroxyl groups and chemisorbed water. An examination of the adsorbent before and after sorption reaction possibly provides information regarding the surface. We can find a group that might have participated in the adsorption reaction and also indicates the surface sites on which adsorption has takes place. After the adsorption of dyes, there is a shift in the peak at 3319.21 cm^{-1} and the band at 1736.71 cm^{-1} disappears.

Fig.4.4.2. IR Spectrum of EY adsorbed passion fruit peel

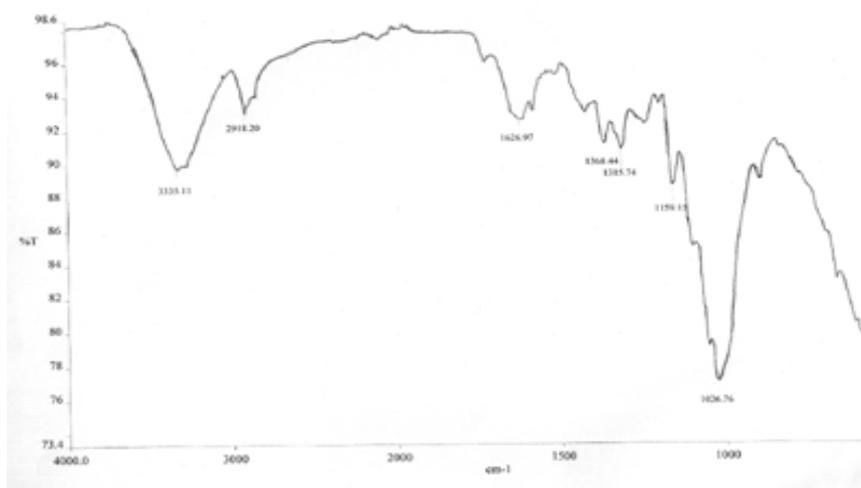
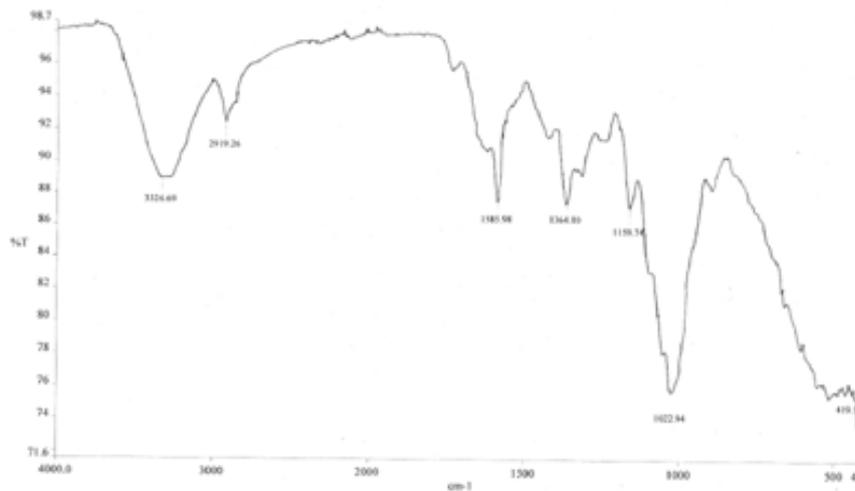


Fig.4.4.3. IR Spectrum of MG adsorbed passion fruit peel



Additional bands corresponding to the dyes appear in the region 1585-1626 cm⁻¹. It was found that the spectra of treated sorbents differ significantly from the spectrum of the “parent” (untreated) material, suggesting that the treatment procedures change the peel structure substantially.

The surface morphology of passion fruit peel was visualized via scanning electron microscopy (SEM), being obtained using a JSM-840 JEOL microscope of JEOL Techniques LTD, Japan at 2000X magnification.

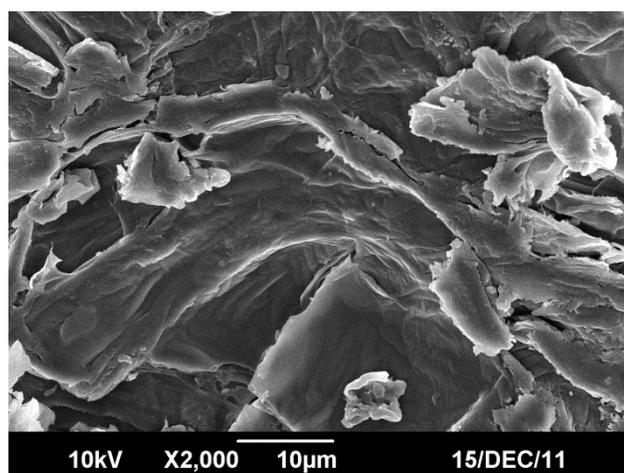
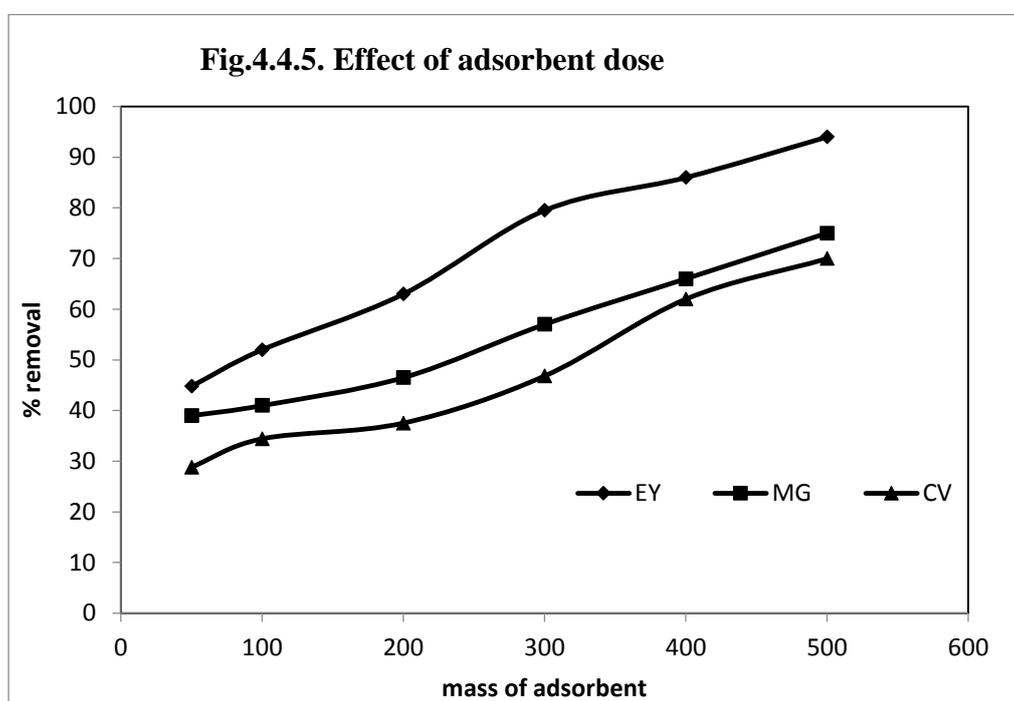


Fig.4.4.4. SEM Photograph of Passion fruit peel powder

Examination of SEM micrographs of the passion fruit peel particles showed rough areas of the surface of the powder (Figure 4.4.4.).

4.4.2. Effect of adsorbent dose

The effect of adsorbent dose was also investigated for the removal of dyes from aqueous solution. The experiments were carried out with adsorbent dose varied from 50-500 mg with keeping other parameters are constant. The removal of dyes was found to be 44.5-94%, 39-75%, 28.5-70% in case of Eosin yellow, Malachite green, crystal violet (fig 4.4.5). The increase in removal of dyes with adsorbent dose is due to the introduction of more binding sites for adsorption.

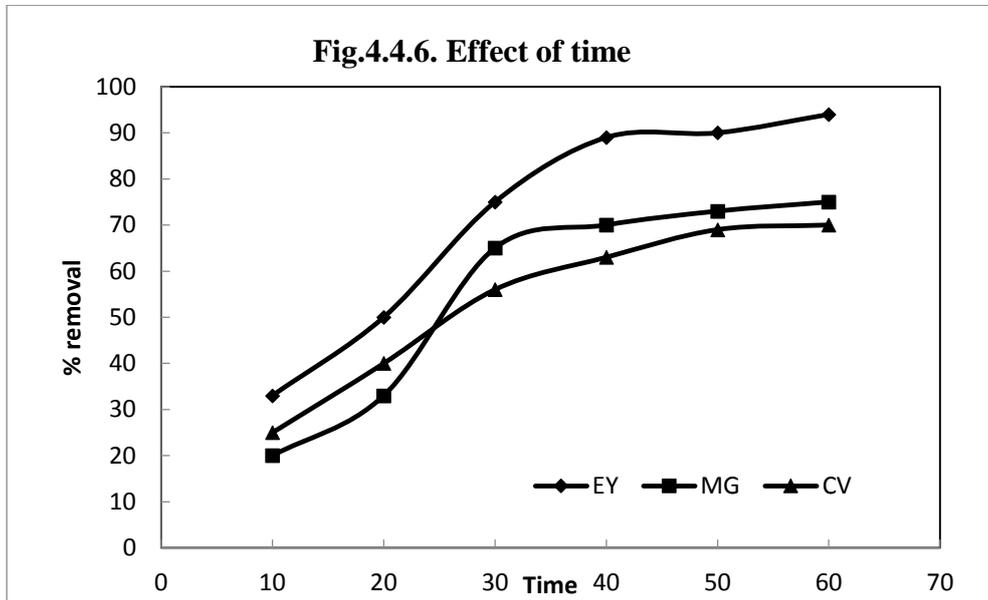


The percentage removal of Eosin yellow is higher than that of Malachite green and Crystal violet. The percentage removal of Malachite green lies between Eosin yellow and Crystal violet. The optimum adsorbent dose was found to be 400mg.

4.4.3. Effect of contact time

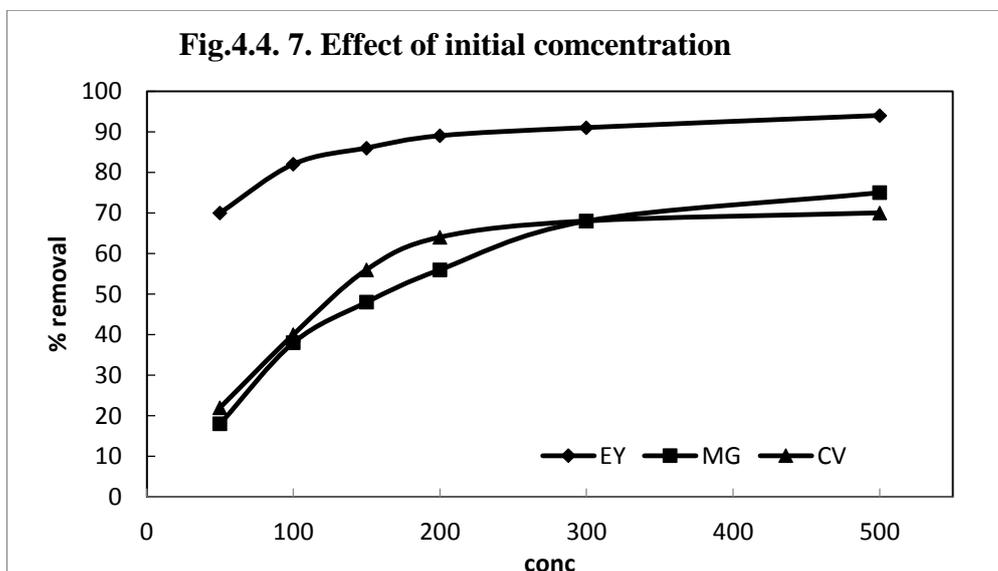
The time dependent behavior of dye adsorption was examined by varying the contact time between adsorbate and adsorbent in the range of 10-60minute. The concentrations of dyes were kept as 500ppm while the amount of adsorbent added was 500mg. The fig 4.4.6. shows that the equilibrium between dyes and the adsorbent was attained within 40 minute. Therefore a 40 minute shaking time was found to be

appropriate for maximum adsorption and was used in all subsequent experiment. The removal of direct dyes by adsorption increased with time and attained a maximum value in 40 min and there after it remained constant. The figure shows that the % removal of EY (500 ppm) is higher than that of other two dyes (Crystal violet and malachite green).



4.4.4. Effect of initial concentration

The effect of concentrations of dyes (50,100,150,200,300,500 ppm) have been also tested with constant dose of adsorbent at 60 min of shaking time. The removal of dyes increased from 70–94% for Eosin yellow, 18-75% for Malachite green and 22-70% for crystal violet.



The plot reached a maximum value and remains constant. The adsorption attains equilibrium within 300 ppm. The results indicated that the adsorption of dyes is much dependent on concentration of solution.

4.4.5. Equilibrium study

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir and Freundlich isotherms. These isotherms relate dye uptake per unit mass of adsorbent, q_e , to the equilibrium adsorbate concentration in the bulk fluid phase C_e .

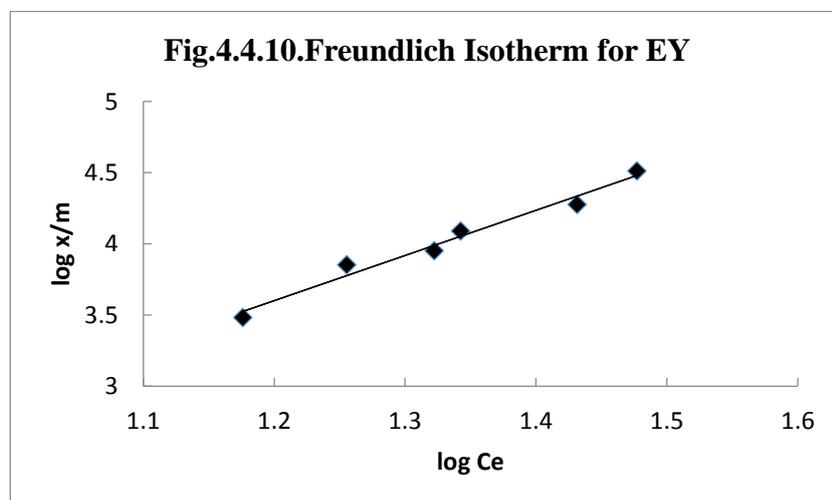
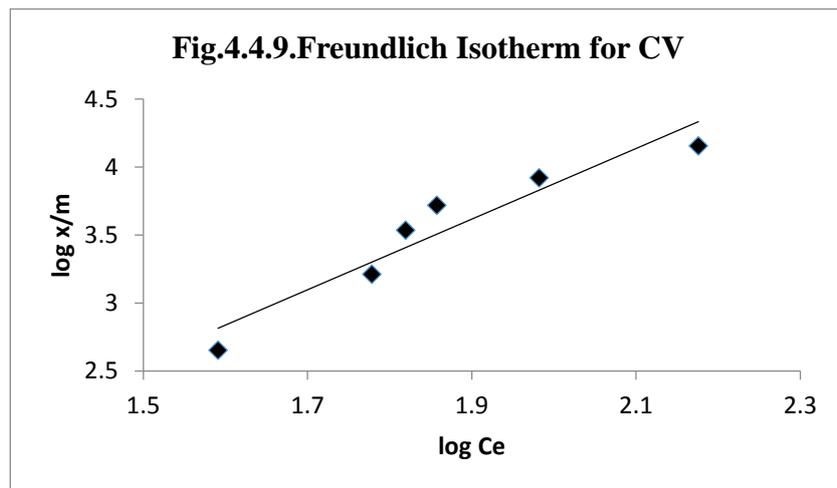
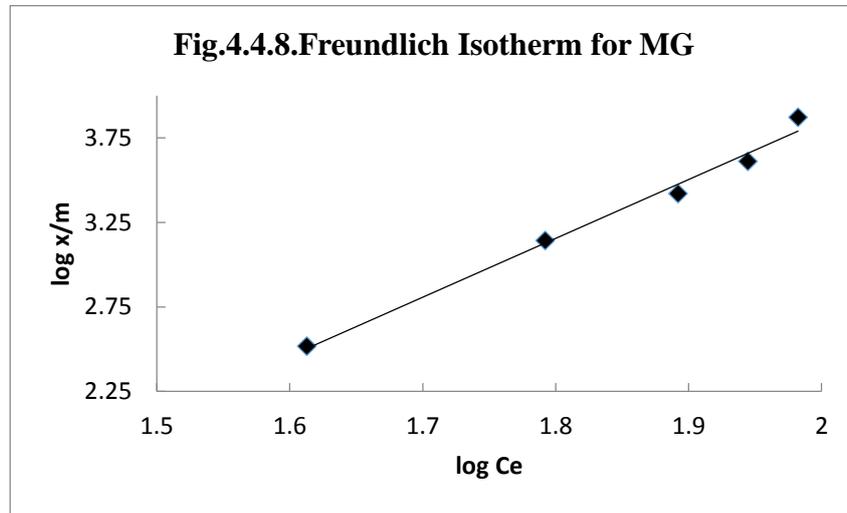
The parameters obtained from the different isotherm models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. According to the obtained data for the model parameters it is seen that Freundlich equilibrium model is favourable. Taking into consideration the values of the coefficient of correlation as criteria for goodness of fit, for most investigated systems the Freundlich equation gives a better correlation between the theoretical and experimental data for the whole concentration range when compared with Langmuir equations.

Table 4.4.1. Kinetic parameters for Freundlich Isotherm

Dyes	Statistical parameter constants			
	r	R ²	K	n
Malachite green	0.9942	0.9734	0.00335	0.3152
Crystal Violet	0.9522	0.9702	0.00152	0.2901
Eosin Yellow	0.9920	0.9763	0.6246	0.3175

The Freundlich constant, n also indicates the degree of favorability of adsorption. The values of K and n are obtained from the intercept and slope of the graph plotted between $\log q_e$ versus $\log C_e$ (Fig.4.4.8-4.4.10). The values of n lie between 0 and 1 (Table 4.4.1), indicated that the adsorption is favourable with the Freundlich isotherm model. The similar results were earlier reported by the other investigators. Hence it should be noted

that the Isotherm constants are important in understanding the adsorption mechanism and their subsequent application for prediction of some important design parameters.

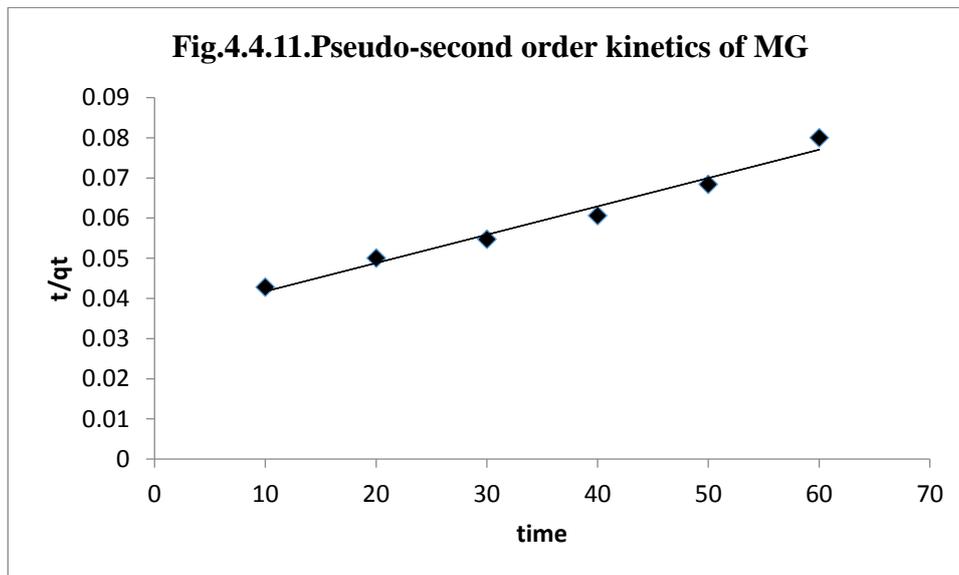


4.4.6. Kinetic Study

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second order equations are applied to model the kinetics of dye adsorption onto passion fruit peel powder. The pseudo-first-order rate equation is given as

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t$$

where q_t and q_e are the amount adsorbed (mg/g) at time t , and at equilibrium respectively and k_{ad} is the rate constant of the pseudo-first-order adsorption process (min^{-1}). Straight line plots of $\log(q_e - q_t)$ against t were used to determine the rate constant, k_{ad} , and correlation coefficients, R^2 , for different dye concentration. But it was seen that adsorption of dyes on passion fruit peel powder did not follow pseudo first-order kinetics compare with the correlation coefficient of pseudo second-order kinetics.



The pseudo-second-order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t$$

where $h = kq_e^2$ ($\text{mg g}^{-1}\text{min}^{-1}$) can be regarded as the initial adsorption rate as $t \rightarrow 0$ and k is the rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1}\text{min}^{-1}$). The plot t/qt versus t should give a straight line if pseudo-second-order kinetics is applicable and q_e , k and h can be determined from the slope and intercept of the plot, respectively. The plots of the linearized form of the pseudo second-order by passion fruit peel powder are shown in Fig. 4.4.11-13.

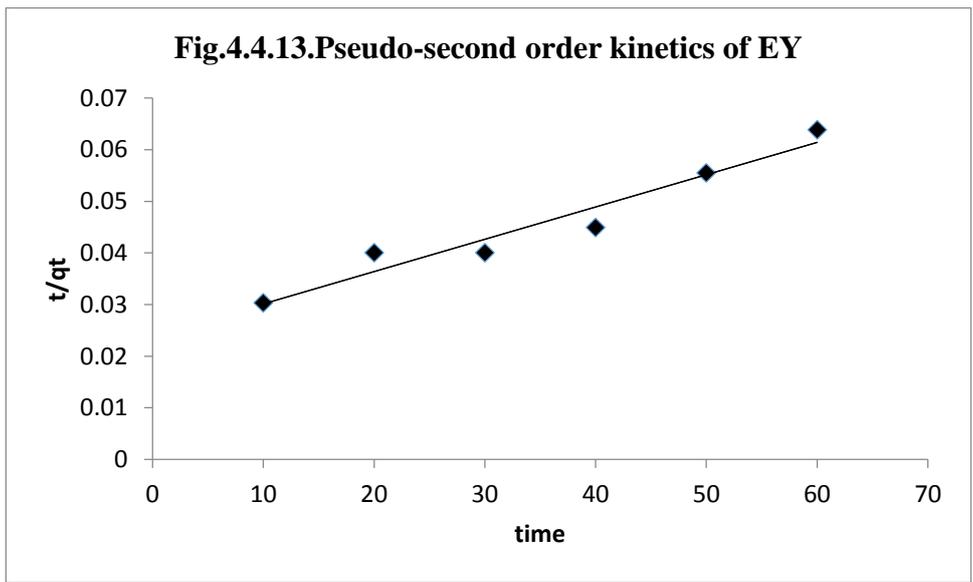
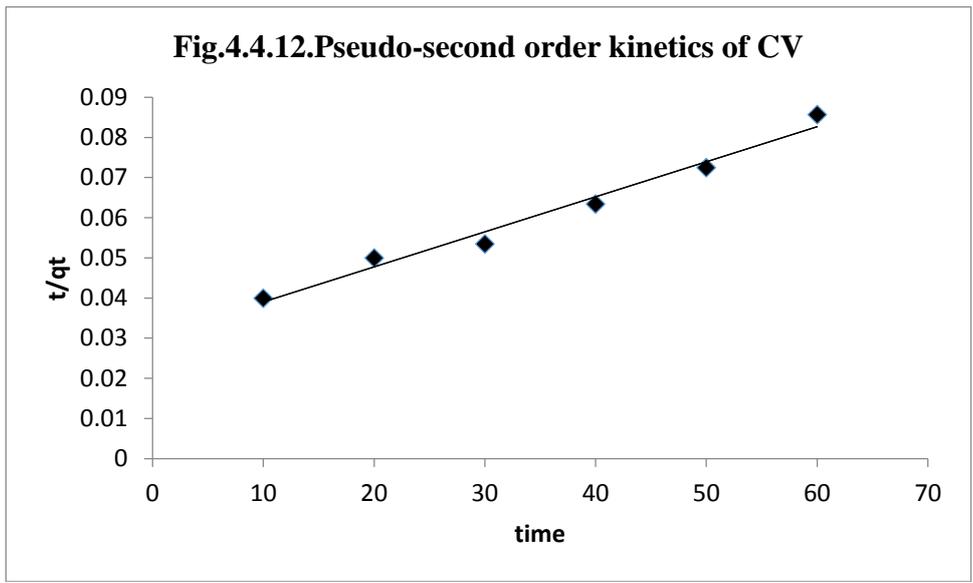


Table.4.4.2. Pseudo-second order parameters for adsorption of dyes

Dyes	Statistical parameter constants			
	r	R ²	q _e	K _{ad}
Malachite green	0.9884	0.9770	1428.57	28.82
Crystal Violet	0.9892	0.9784	1111.11	33.00
Eosin Yellow	0.9907	0.9823	1666.67	41.84

The plot of t/q_t versus t for pseudo-second-order model yields very good straight lines (correlation coefficient, $R^2 > 0.97$) as compared to the plot of pseudo-first order.

4.5. Used Black Tea as Low Cost Adsorbent

4.5.1. Characterisation of the adsorbent

FTIR spectra (Fig.4.1.a-d) were carried out and a broad absorption peak at 3285.32 cm^{-1} is indicative of bonded hydroxyl group. A peak observed at 1626.36 cm^{-1} can be assigned to $>\text{C}=\text{O}$ group. A peak at 1516.12 cm^{-1} indicates secondary amino group. The peak at 1447.4 cm^{-1} may be due to symmetric C-H stretching and C-O stretching of ether group is observed due to peak at 1032.56 cm^{-1} .



Fig. 4.5.1. IR spectrum of used black tea powder

An examination of the adsorbent before and after sorption reaction possibly provides information regarding the surface a group that might have participated in the adsorption reaction and also indicates the surface sites on which adsorption has takes place.

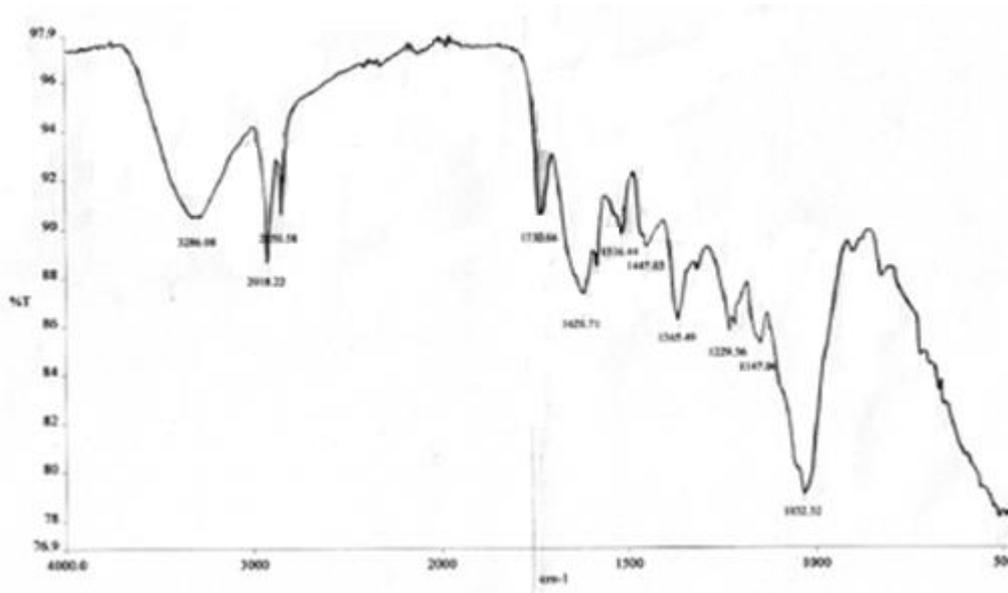


Fig. 4.5.2. IR spectrum of used black tea powder

It was found that the spectra of treated sorbents did not differ significantly from the spectrum of the “parent” (untreated) material, suggesting that the treatment procedures did not change substantially the tea powder structure.

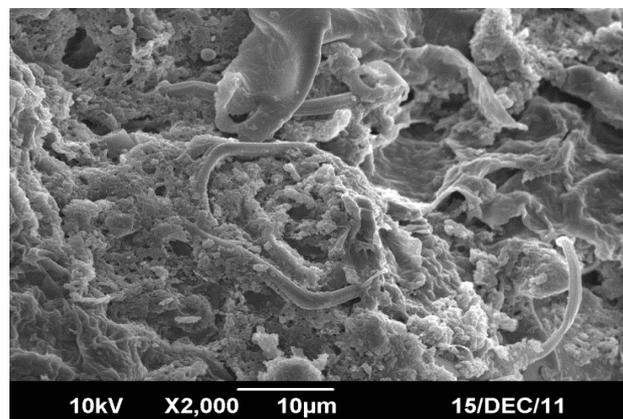


Fig.4.5.3. SEM of used black tea

SEM (Figure 4.5.3.) revealed that the surface of adsorbent is rough and almost non compact in nature. Used black tea waste has considerable number of pores suitable for physisorption.

4.5.2. EFFECT OF ADSORBENT DOSAGE

The effect of the adsorbent dose was studied at room temperature by varying the sorbent amounts from 50 to 400 mg. For all these runs, initial concentration of dyes was fixed as 500 ppm.

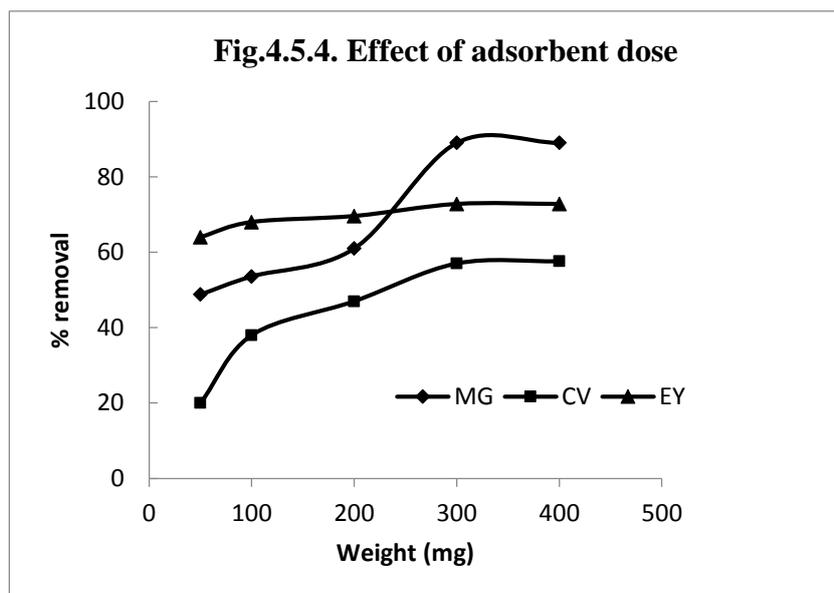
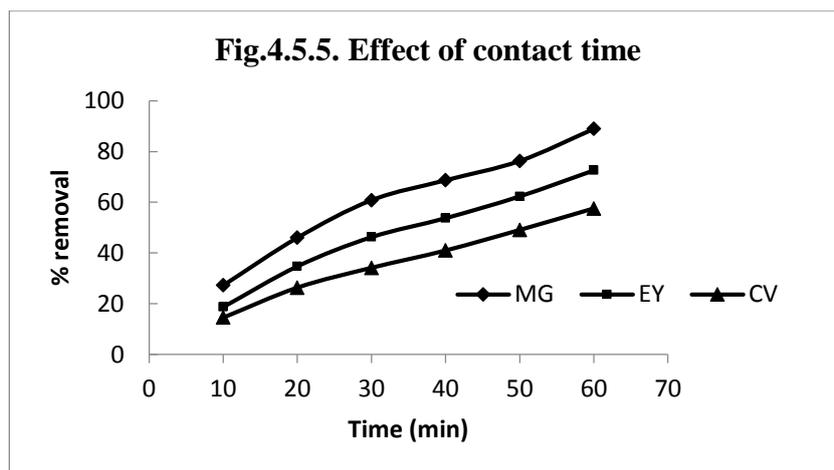


Figure.4.5.4. shows that adsorption of all these dyes increases rapidly with increase in amount of used black tea due to greater availability of the adsorption sites at higher concentration of the adsorbent. Any further addition of the adsorbent beyond 300mg did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles. From the results, it is revealed that within a certain range of initial dye concentration, the percentage of dye adsorption on used black tea is determined by the sorption capacity of the powder.

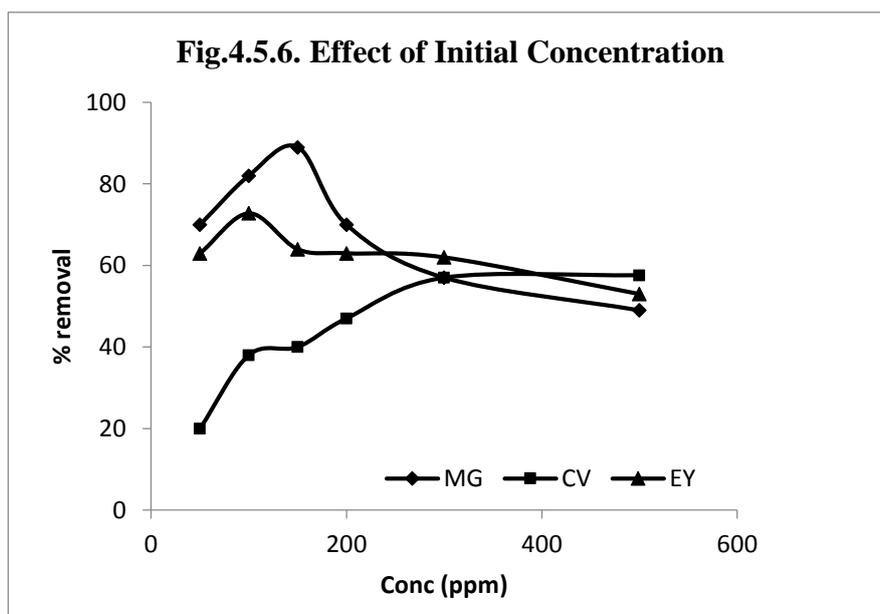
4.5.3. EFFECT OF TIME

Adsorption of dyes was measured at different contact time for three different dyes. The plot (Fig.4.5.5.) reveals that the rate of percentage of dye removal is higher at the beginning. This is probably due to large surface area being available at beginning for the adsorption. The increasing contact time increased the dye adsorption and it remains constant after 60 min.



4.5.4. EFFECT OF INITIAL CONCENTRATION

The effect of initial dye concentration in the range of 50 to 500 ppm on adsorption is shown in figure 4.5.6.



It is seen that removal of dye was dependent on the concentration of dye as the increase in initial concentration increased the dye removal up to 150 ppm for malachite green and 100 ppm for eosin yellow and after that the % removal decreased. In the case of crystal violet it is goes on increasing with increase in initial concentration.

4.5.5. EQUILIBRIUM STUDY

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that

are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir, Freundlich and Temkin isotherms. These isotherms relate dye uptake per unit mass of adsorbent, q_e , to the equilibrium adsorbate concentration in the bulk fluid phase C_e .

4.5.5. a. The Langmuir isotherm

The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane.

The constants in the Langmuir isotherm can be determined by plotting (C_e/q_e) versus (C_e) and making use of equation

$$C_e/q_e = C_e/q_m + 1/q_m K_L$$

where q_m and K_L are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively.

4.5.5. b. The Freundlich isotherm

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of dye adsorbed per unit mass of adsorbent, q_e , and the concentration of the dye at equilibrium, C_e . The logarithmic form of the equation is:

$$\log (x/m) = \log K_f + 1/n \log C_e$$

where K_f and n are the Freundlich constants, the characteristics of the system. K_f and n are the indicators of the adsorption capacity and adsorption intensity, respectively. The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of $\log C_e$ vs. $\log (x/m)$ was employed to generate the intercept value of K_f and the slope of n . The magnitudes of K_f and n show easy separation of MG and EY dyes from the aqueous solution and indicate favourable adsorption whereas the values of K_f and n are very low for CV indicating an unfavorable adsorption.. The intercept K_f value is an

indication of the adsorption capacity of the adsorbent; the slope $1/n$ indicates the effect of concentration on the adsorption capacity and represents adsorption intensity.

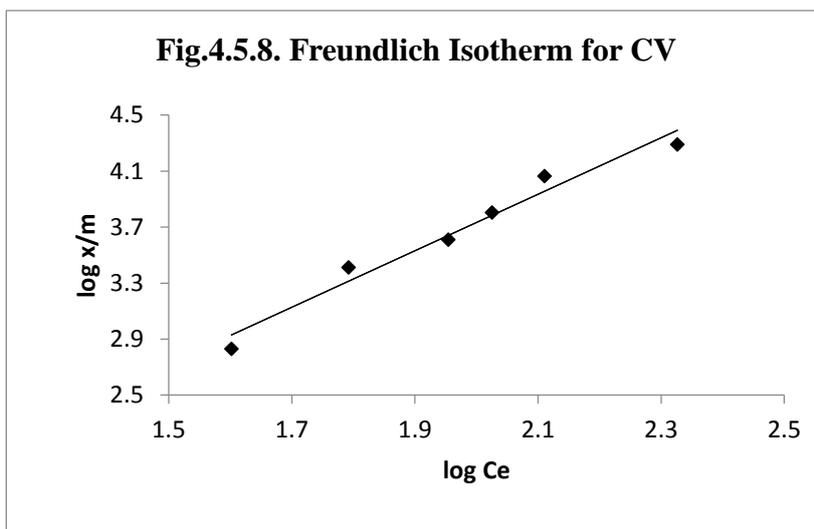
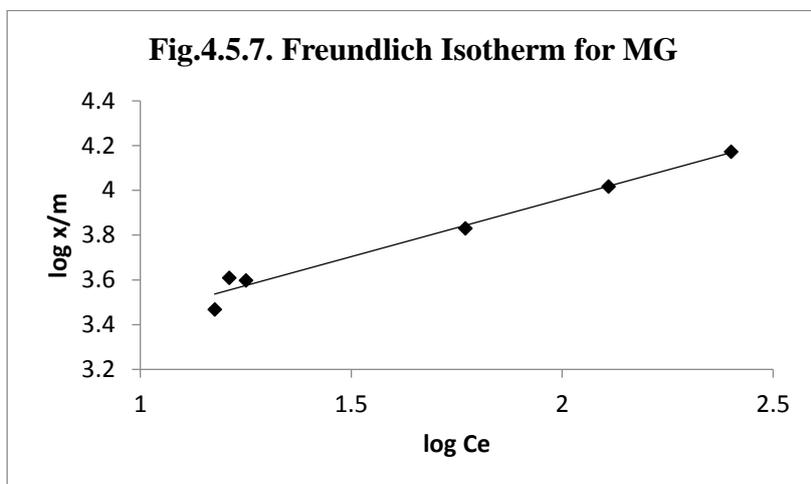
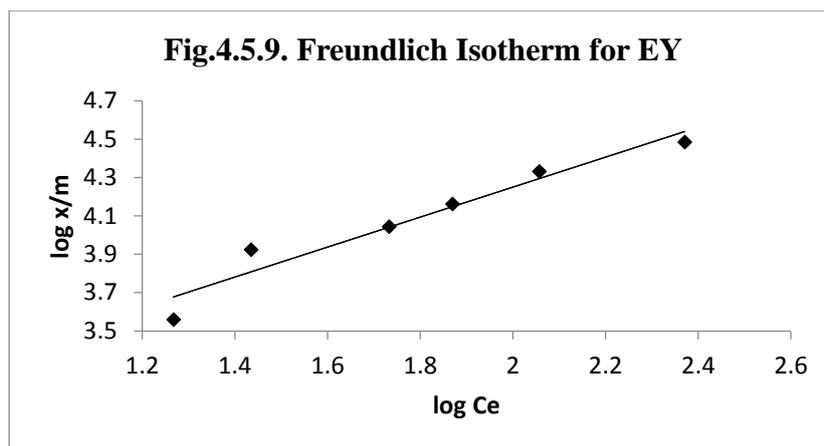


Table 4.5.1. Kinetic parameters for Freundlich Isotherm

Dyes	Statistical parameter constants			
	r	R ²	K	n
Malachite green	0.9885	0.9772	4.901x10 ²	1.9368
Crystal Violet	0.9695	0.9400	0.4988	0.4957
Eosin Yellow	0.9839	0.9680	4.885 x10 ²	1.2820



As seen from Table.4.5.1, n value was found high enough for separation for malachite green and eosin yellow. The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model. Equilibrium study revealed that Freundlich isotherm fitted well with the correlation coefficient of 0.9885 and 0.9839 for MG and EY respectively than Langmuir adsorption isotherm.

4.5.6. Kinetic Study

The rate of removal of dyes by used black tea has been studied as a function of time. Adsorption rate constant study was carried out with the famous Lagergran rate equation.

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t$$

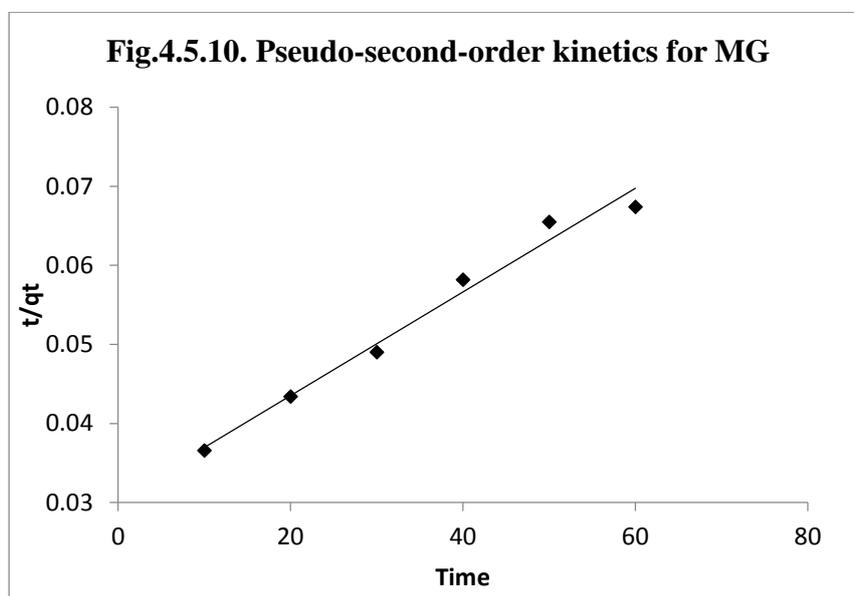
where q_t and q_e are the amount adsorbed (mg/g) at time, t , and at equilibrium respectively and k_{ad} is the rate constant of the pseudo-first-order adsorption process (min^{-1}).

The linear form of Pseudo second order kinetic model was also applied on the data. The pseudo-second-order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t$$

where $h = kq_e^2$ ($\text{mg g}^{-1}\text{min}^{-1}$) can be regarded as the initial adsorption rate as $t \rightarrow 0$ and k is the rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1}\text{min}^{-1}$). The plot t/q_t

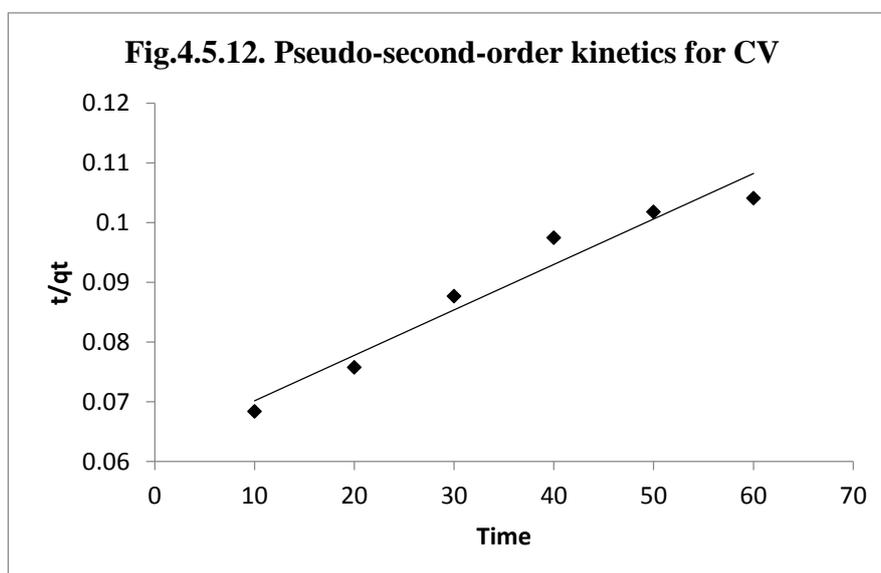
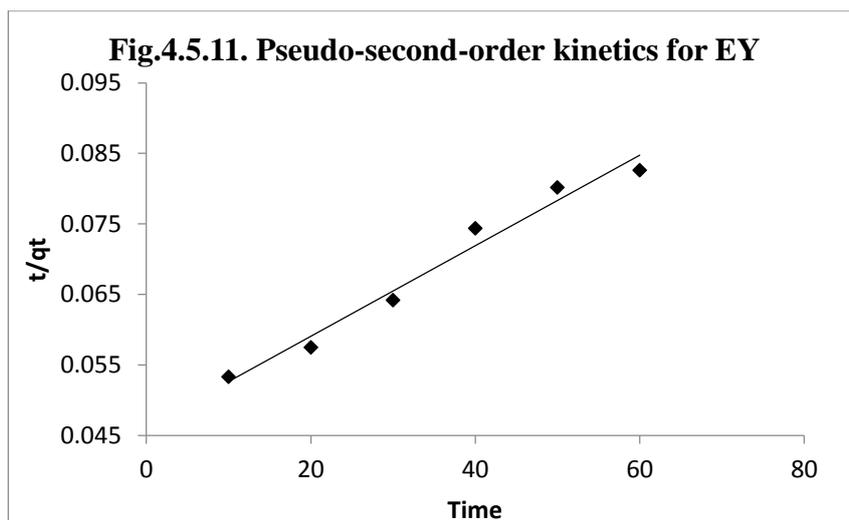
versus t should give a straight line if pseudo-second-order kinetics is applicable and q_e , k and h can be determined from the slope and intercept of the plot, respectively. The plots of the linearized form of the pseudo second-order by used black tea powder are shown in Fig. 4.5.10-12.



A linear plot is obtained for all the dyes suggesting the applicability of pseudo second order model on the data well. The values of Rate constant and q_e was calculated and has been given in table 4.5.2.

Table.4.5.2. Pseudo-second order parameters for adsorption of dyes

Dyes	Statistical parameter constants			
	r	R ²	q _e	K _{ad} (x10 ⁻⁵)
Malachite green	0.9905	0.9812	1666.66	1.1842
Crystal Violet	0.9873	0.9742	1250.00	1.0220
Eosin Yellow	0.9756	0.9519	1428.57	1.0606



The determinant coefficient (square of correlation coefficient) for the pseudo-second-order model was 0.9812, 0.9742 and 0.9512 for MG, EY and CV respectively being significantly higher than that for the pseudo first-order model. It suggests that the dye adsorption process of the spent tea leaf adsorbent was more fitted to the pseudo-second-order model than the pseudo-first-order model.

4.6. Saw Dust as Low Cost Adsorbent

4.6.1. Characterisation of the adsorbent

The IR spectral analysis is important to identify the characteristic functional groups on the surface of the adsorbent, which are responsible for adsorption of heavy metal ions. The IR spectrum of sawdust was recorded to obtain the information

regarding the stretching vibrations of the functional groups which are involved in the adsorption of the adsorbate molecules. The IR spectrum of sawdust before and after metal ion adsorption are shown in the figure 4.6.1-3. The IR spectral analysis of sawdust shows distinct peak at 558.27, 1047.54, 1729.3 and 3332.65 cm^{-1} . The peak observed at 558.2 and 1047.54 may be assigned to the presence of vinyl compound ester group respectively. The peak observed at 1729 cm^{-1} confirm the presence of carbonyl group. the peak at 3332.65 cm^{-1} reveals alkyne stretching vibration.

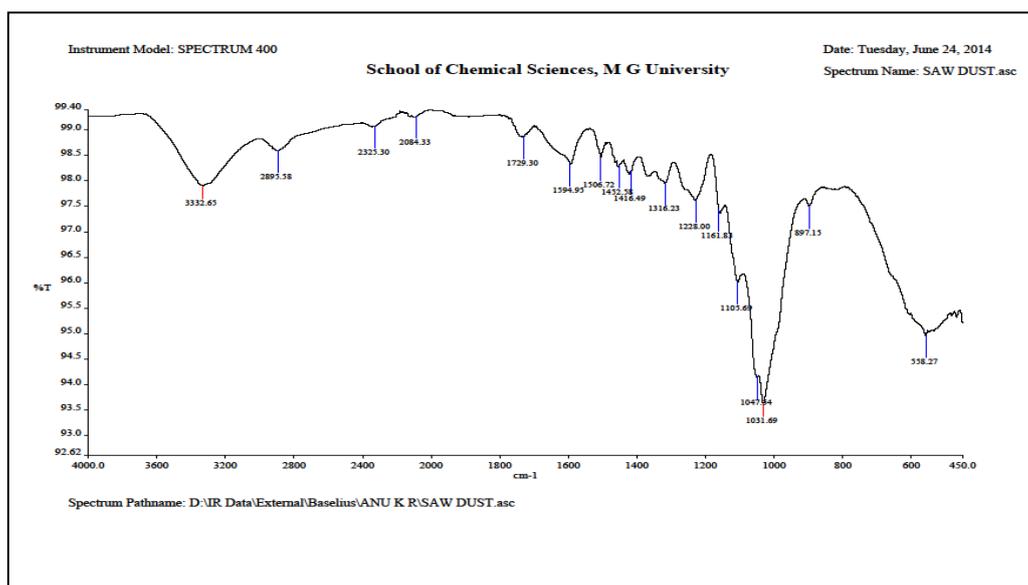


Fig 4.6.1. IR spectrum of saw dust

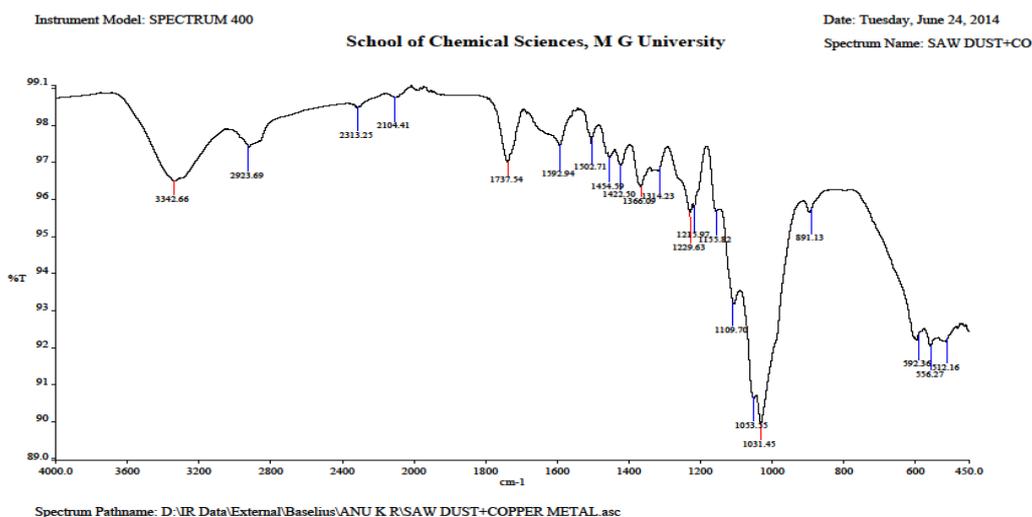


Fig 4.6.2. IR Spectrum of sawdust loaded with Cu

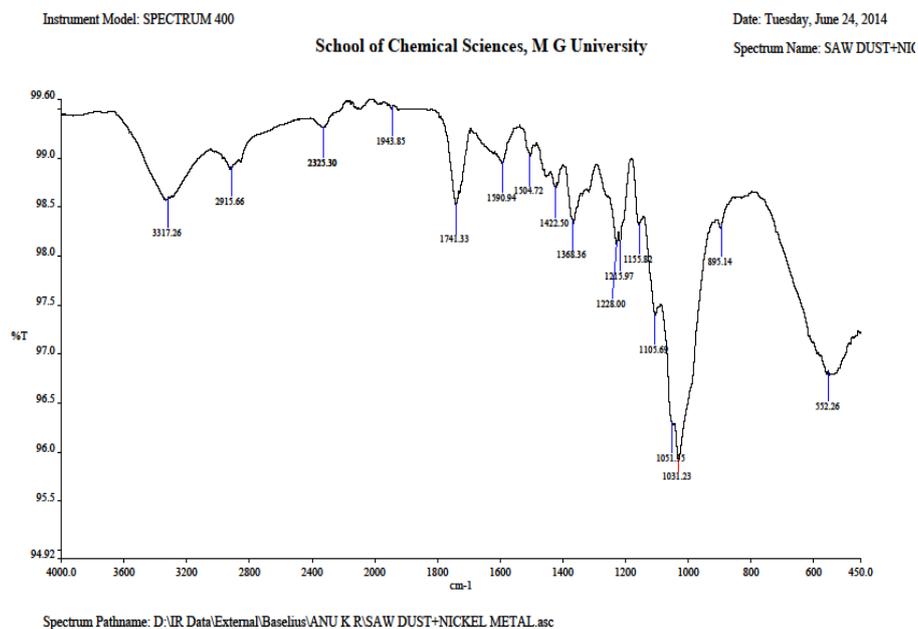


Fig 4.6.3. IR Spectrum of sawdust loaded with Ni

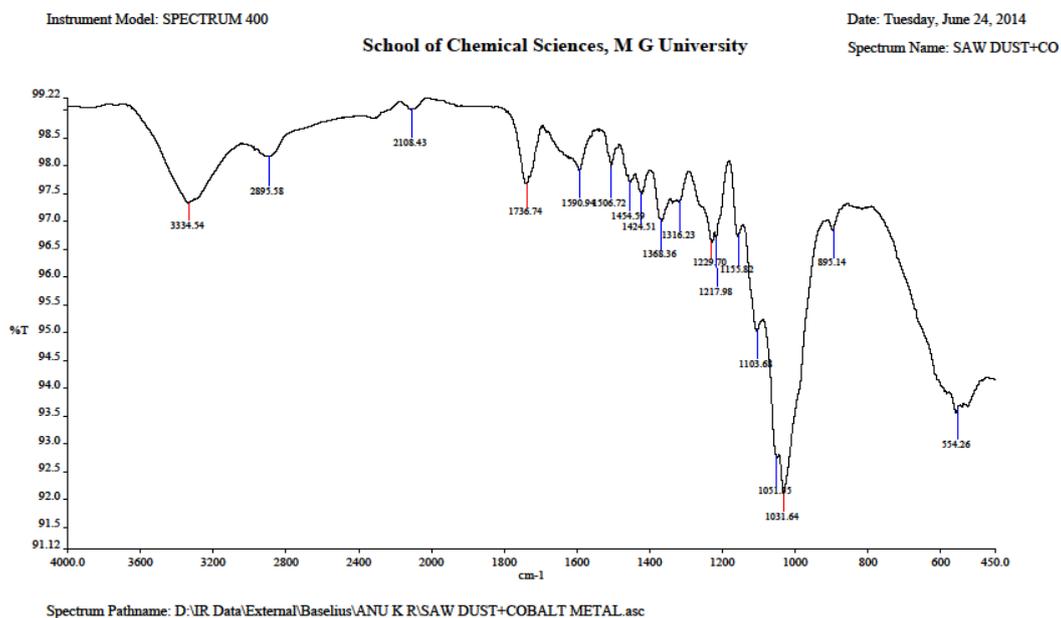


Fig 4.6.4. IR spectrum of saw dust loaded with Co

SEM analysis is another useful tool for the analysis of the surface morphology of an adsorbent. The porous and irregular surface structure of the adsorbent can be clearly observed in SEM images shown in figure 4.6.5.

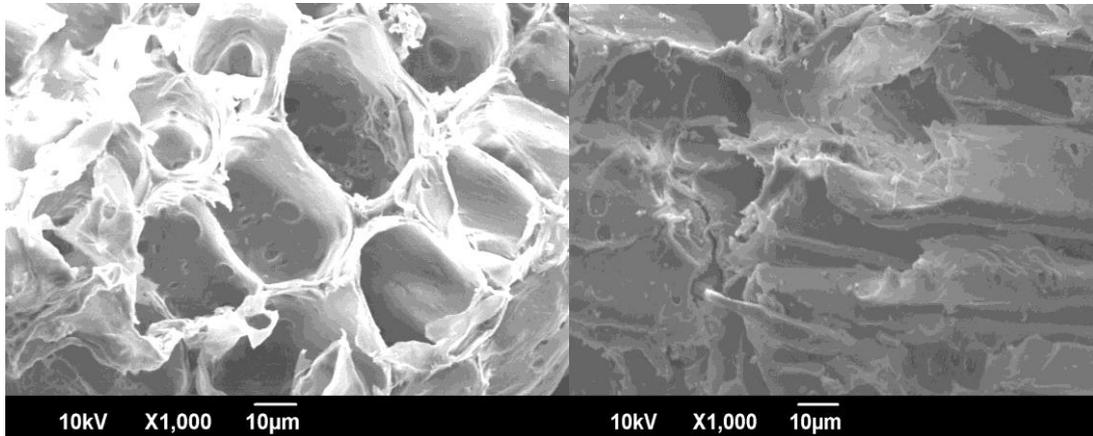
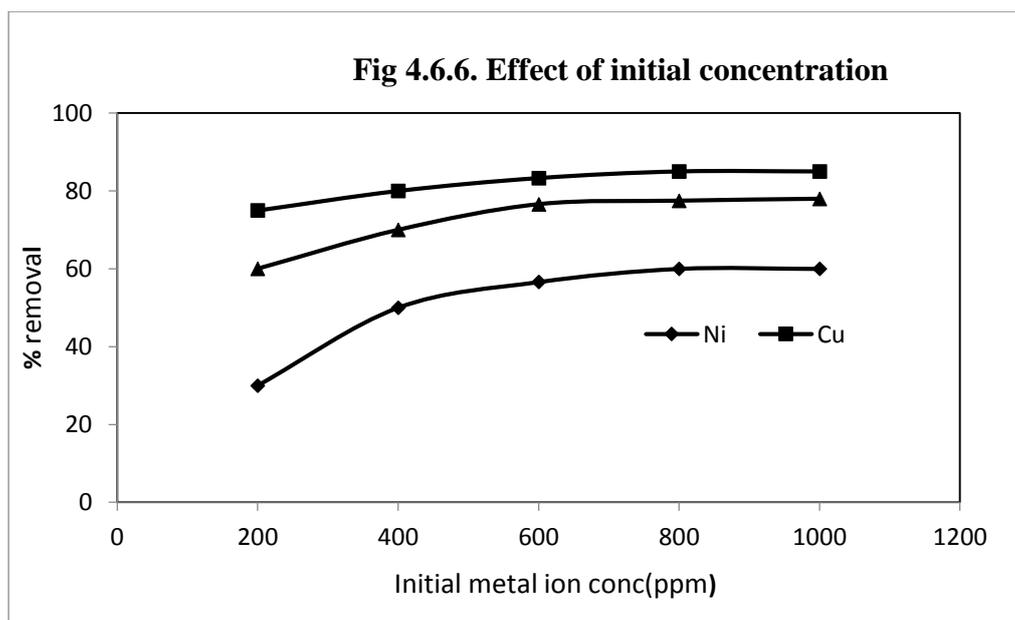


Fig 4.6.5. SEM of saw dust and Cu loaded saw dust

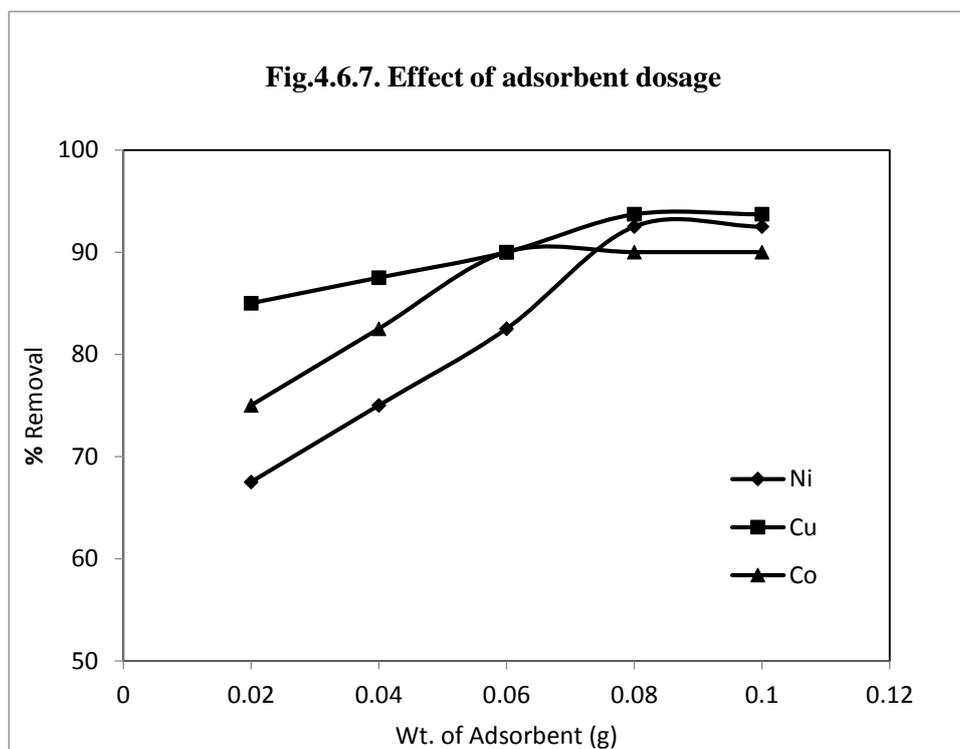
4.6.2. Effect of initial concentration

Initial metal ion concentration is one of the effective factors in removal efficiency. Fig.4.6.6 depicts the effect of increase in initial metal ion concentration on the adsorption of the various metal ions onto saw dust adsorbent. The strong affinities of Cu, Ni & Co the saw dust give concentration to a marginal variation in % adsorption with increase in initial metal ion.



4.6.3. Effect of adsorbent dosage

From fig.4.6.7, it is apparent that by increasing the adsorbent dose the removal efficiency of each ion increases. This is readily understood from the fact that the number of available adsorption site increases by increasing the adsorbent dose and therefore, result in the increase in the removal efficiency or the % adsorption of the respective ion.

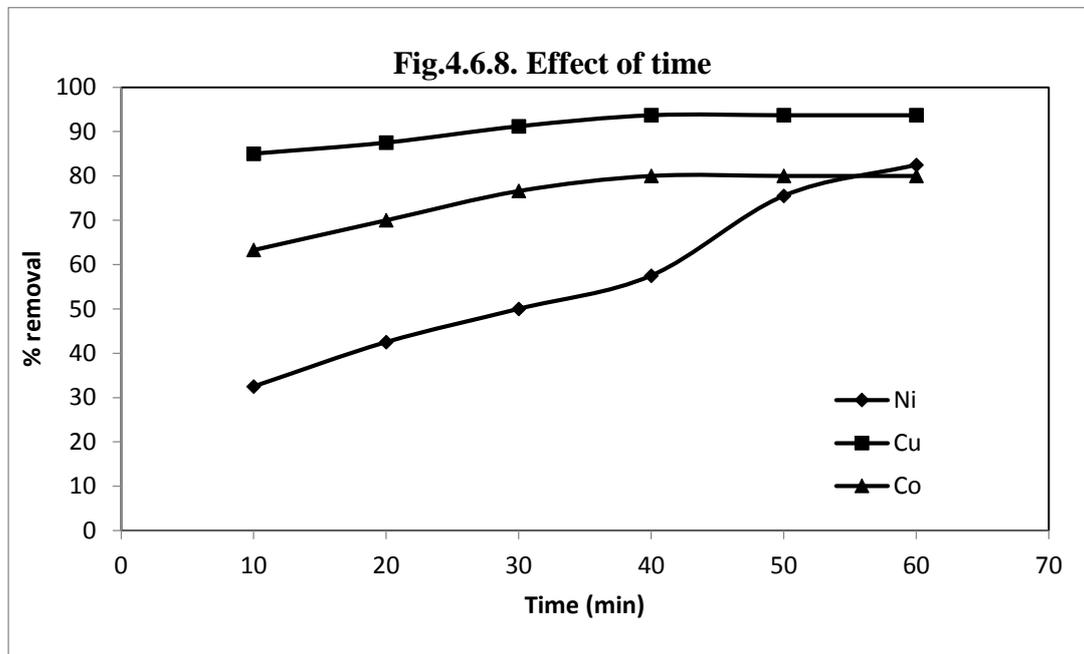


Also, at a low adsorbent dose, e.g. 2g, the available sorption site were quite insufficient compare with the large amount of adsorbate ions in the solution, resulting in low removal efficiency. However, at a higher adsorbent dose, e.g. 8g, the sorption sites were sufficient thereby resulting in a rapid removal of the different adsorbates. The adsorption order of the adsorbate on the saw dust was observed to follow the pattern $Cu > Co > Ni$.

4.6.4. Effect of agitation time

To establish an appropriate contact time between the sawdust and metallic ion solution, adsorption capacities of metal ion were measured as a function of time (Fig.4.6.8). The plot reveals that the rate of the percentage of HMI removal is higher at the beginning. That is probably due to the larger surface area of the sawdust being available at beginning for the adsorption of metals. As the surface adsorption sites

become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. The rate of heavy metal ion removal was attained after approximately 50 min stirring.



4.6.5. Isotherm data analysis

The parameters obtained from the different isotherm models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. Langmuir and Freundlich isotherms are used for fitting the experimental data in adsorption studies to understand the extent and degree of favorability of adsorption. According to the obtained data for the model parameters it is obvious that Freundlich equilibrium model is favourable. Taking into consideration the values of the coefficient of correlation as criteria for goodness of fit, for most investigated Systems the Freundlich equation gives a better correlation between the theoretical and experimental data for the whole concentration range when compared with Langmuir equations.

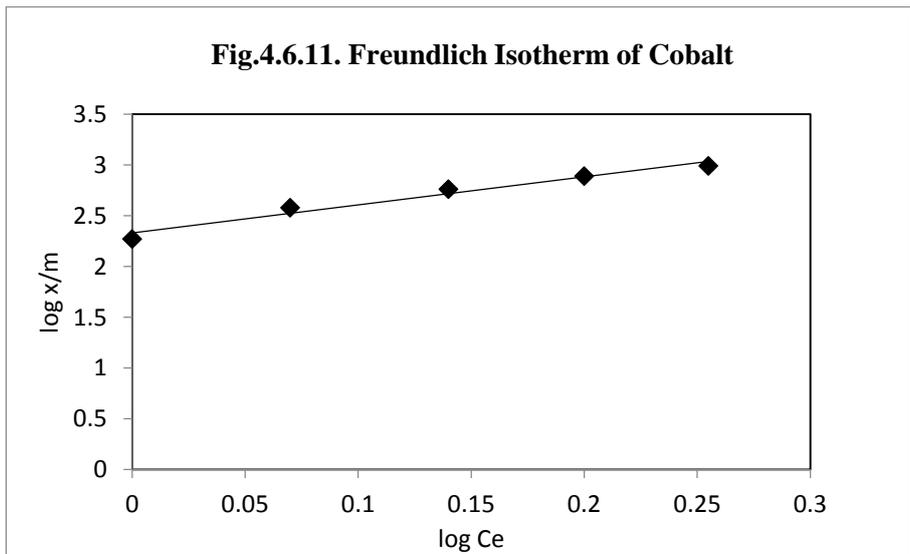
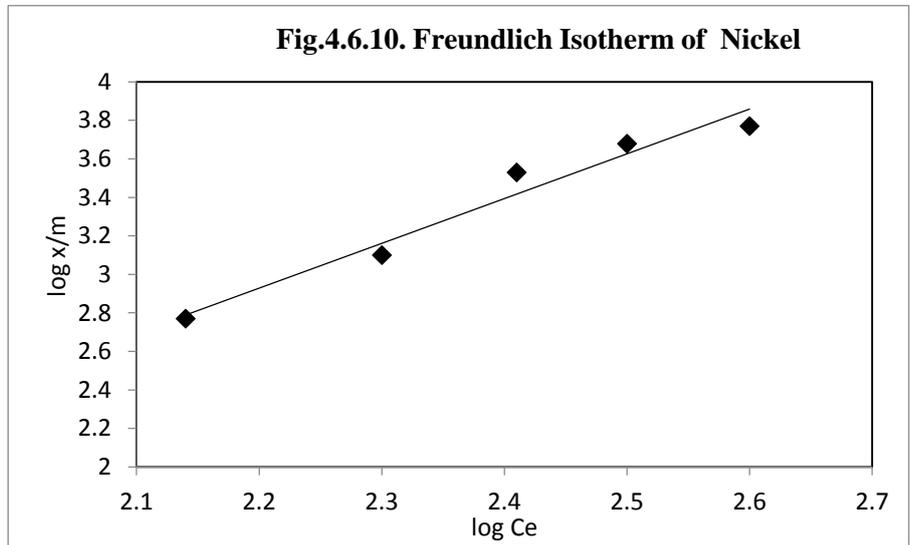
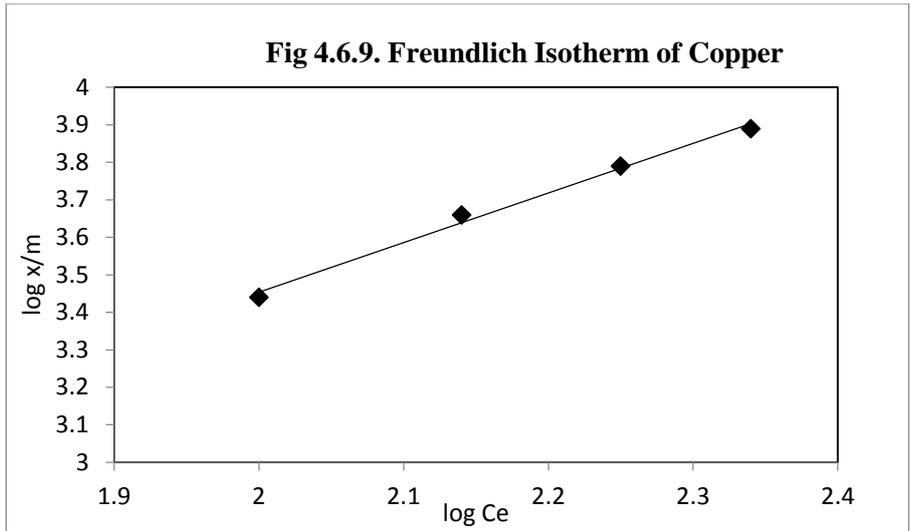


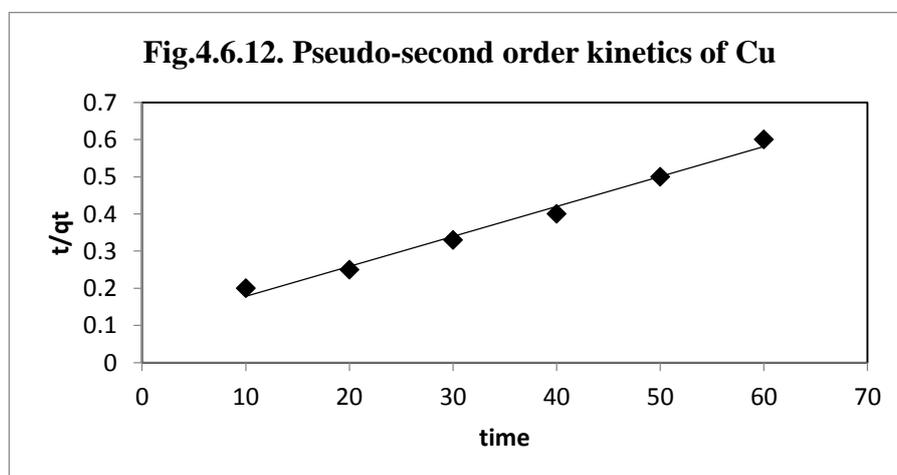
Table.4.6.1. Kinetic parameters for Freundlich isotherm

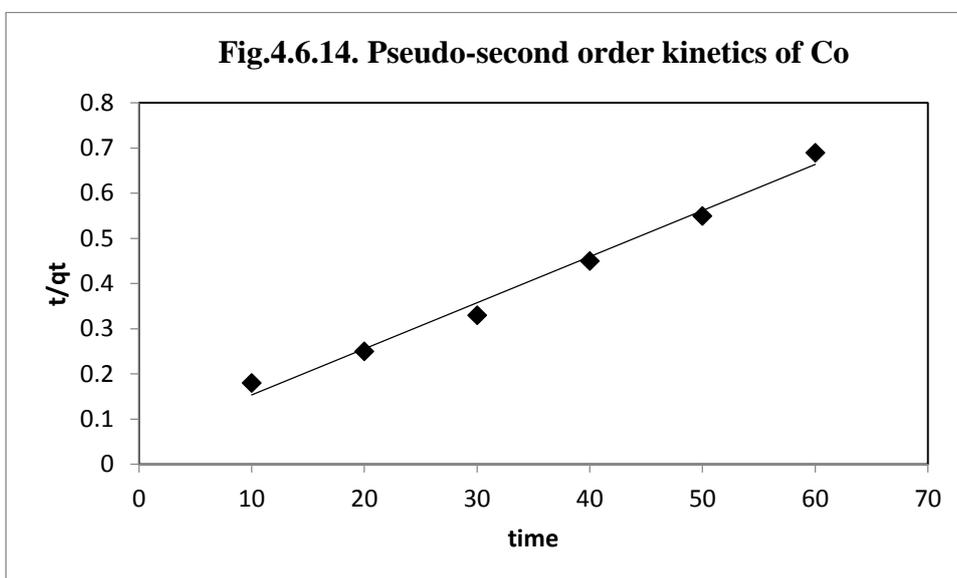
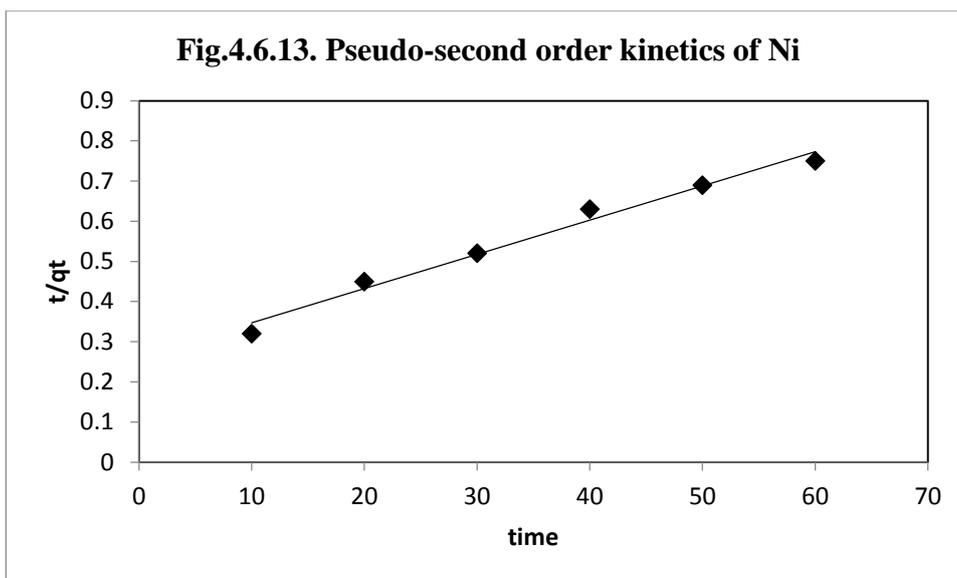
Metals	Statistical Parameter Constant			
	r	R ²	K	n
Copper	0.9685	0.992	6.48	0.757
Nickel	0.9827	0.961	6.54	0.43
Cobalt	0.9832	0.966	2.14	0.362

The Freundlich constant, n also indicates the degree of favorability of adsorption. The Freundlich constant, n have values lying in the range of 1 to 10 for classification as favorable adsorption. A smaller value of (1/n) indicates a stronger bond between adsorbate and adsorbent while a higher value for k indicates rate of adsorbate removal is high. Hence it should be noted that the Isotherm constants are important in understanding the adsorption mechanism and their subsequent application for prediction of some important design parameters.

4.6.6. Adsorption Kinetics

Several steps can be used to examine the controlling mechanism of adsorption process such as chemical reaction, diffusion control and mass transfer; kinetic models are used to test experimental data from the adsorption of Cu, Ni onto Co. The kinetics of metal adsorption onto sawdust is required for selecting optimum operating conditions for the full-scale batch process.





The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes.

Table.4.6.2. The rate constant for Pseudo-second order adsorption

Metals	Statistical Parameter Constant			
	r	R²	q_e	K_{ad}
Copper	0.9928	0.993	125	6.52x10 ⁻⁴
Nickel	0.976	0.971	125	2.44x10 ⁻⁴
Cobalt	0.982	0.985	100	1.96x10 ⁻³

4.7. Mango Leaf as Low Cost Adsorbent

4.7.1. Characterization of the adsorbents

a) FT-IR spectroscopy

In order to gain better insight into the surface functional groups available on the surface of the different investigated adsorbents, the IR spectra of adsorbent before and after adsorption of dye were recorded as shown in Figs.4.7. 1-3. Mango leaf powder. IR spectrum (Fig.4.1) showed five intense bands, at 3321.28, 2919.05, 1739, 1614.7 and 1032.38 cm^{-1} . The band at 3321.28 and 2919.05 cm^{-1} which refers to (-OH) and identical alkyl group (-CH₂-) respectively. Also the spectrum shows bands at 1739 and 1032.38 cm^{-1} were to be the presence of (C=O) and (-OH), respectively.

An examination of the adsorbent before and after sorption reaction possibly provides information regarding the surface a group that might have participated in the adsorption reaction and also indicates the surface sites on which adsorption has taken place.

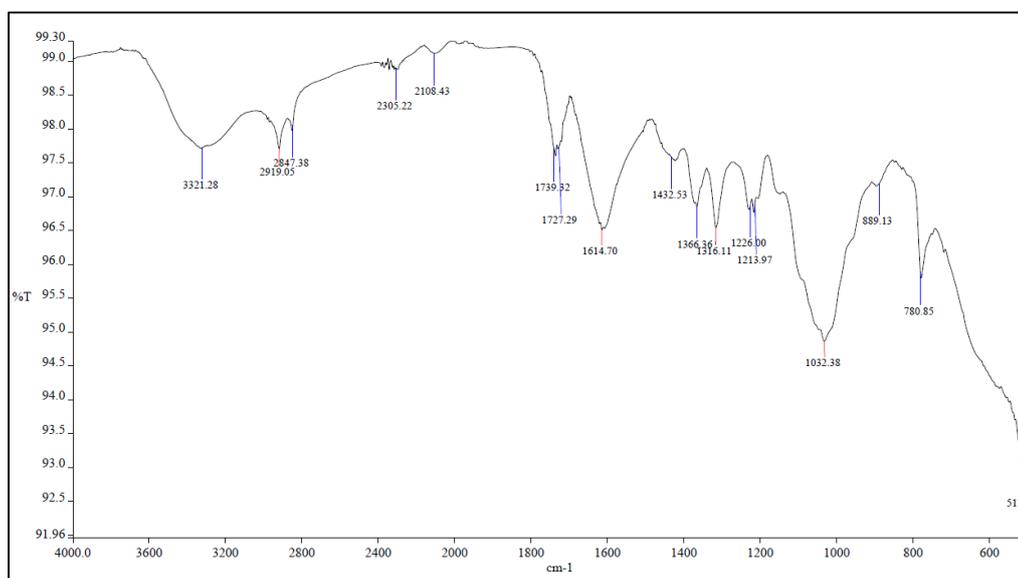


Fig.4.7.1. IR Spectrum of Mango leaf powder

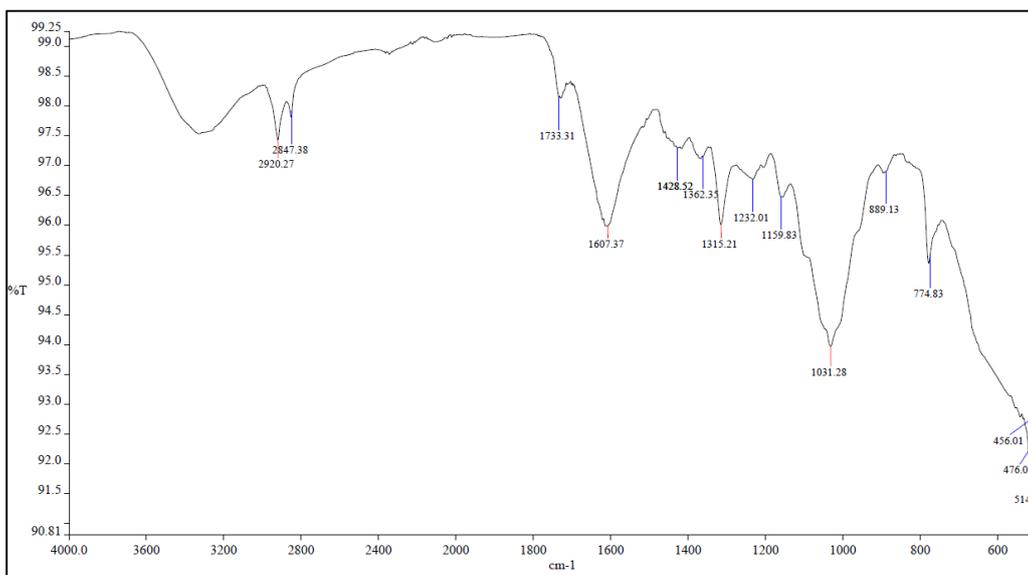


Fig.4.7.2. IR Spectrum of Congo Red adsorbed Mango leaf powder

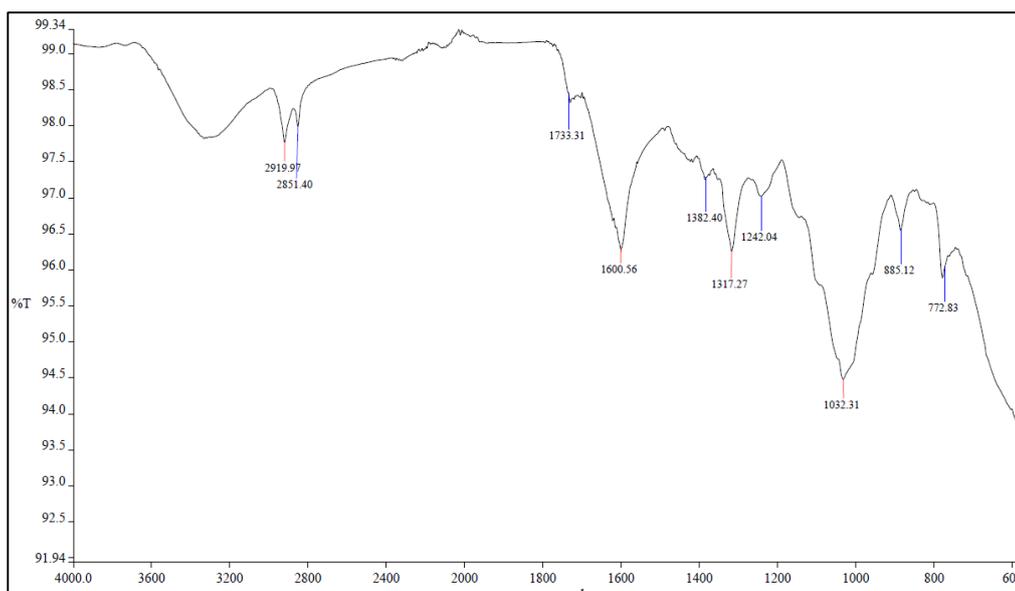


Fig.4.7.3. IR Spectrum of Methylene Blue adsorbed Mango leaf powder

Both spectra show the O-H stretching region at around 3300cm^{-1} . However, a new band at 1733.31cm^{-1} , which corresponds to the MB and CR and one at 1600 and 1607.37cm^{-1} for MB and CR confirms dye adsorption onto the mango leaf powder.

b) SEM analysis

A better understanding of the surface morphology is provided by the Scanning Electron microscopy (SEM). The porous structure of the adsorbent is visible in the micrograph (Fig 4.7.4.). After adsorption, the surface of the adsorbent becomes rough and rigid and the voids are absent.

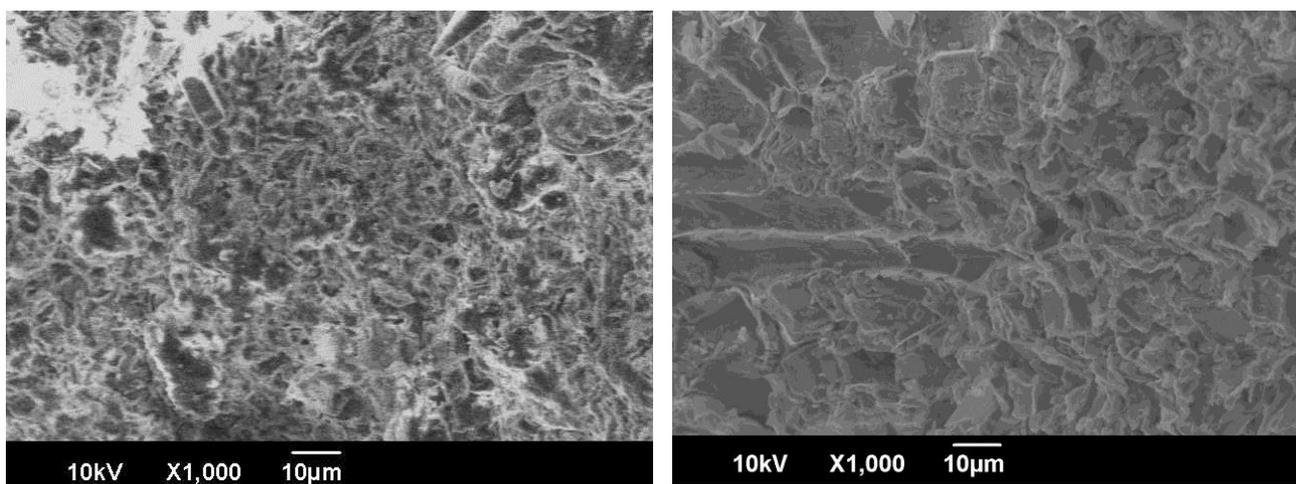


Fig.4.7.4. SEM of mango leaf powder before and after adsorption

The maximum wavelengths (λ_{\max}) and extinction coefficients(ϵ) of prepared dye solutions are given in Table 4.7.1.

Table.4.7.1. Characterization of dyes

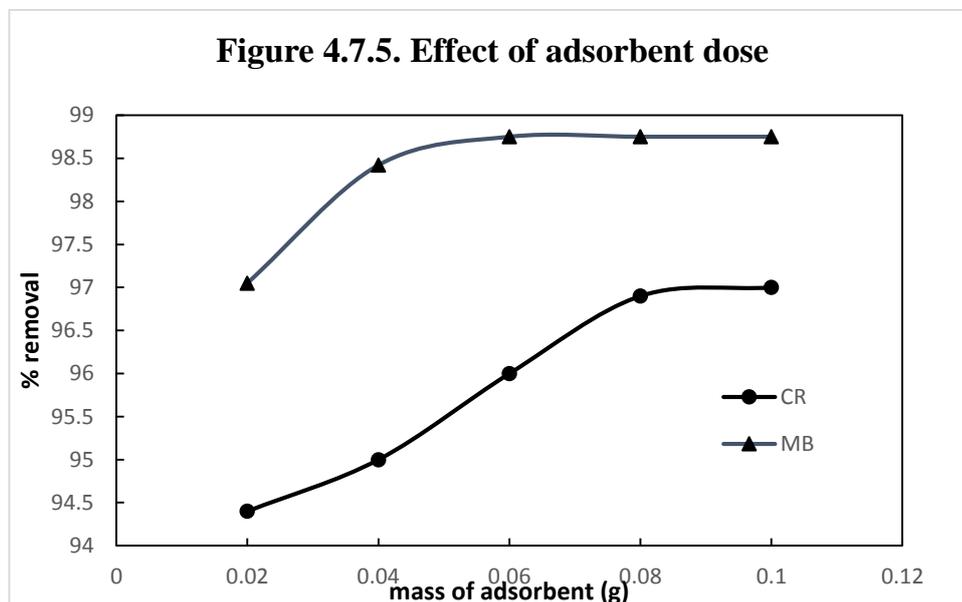
Dye	CAS No	Colour index No.	F.W. (gmol^{-1})	λ_{\max} (nm)	ϵ ($\text{dm}^3/\text{mol}\cdot\text{cm}$)
Methylene Blue	61-73-4	52015	319.85	661	73044
Congo Red	573-58-0	22120	696.67	497	89500

4.7.2. ADSORPTION STUDIES

4.7.2. 1. Effect of adsorbent dose

The effect of the adsorbent dose was studied at room temperature by varying the sorbent amounts from 20 to 100mg. For all these runs, initial concentration of dyes was fixed as 100 mg/L. Figure 4.7.5. shows that adsorption of all the two dyes increases rapidly with increase in the amount of mango leaf powder due to greater availability of

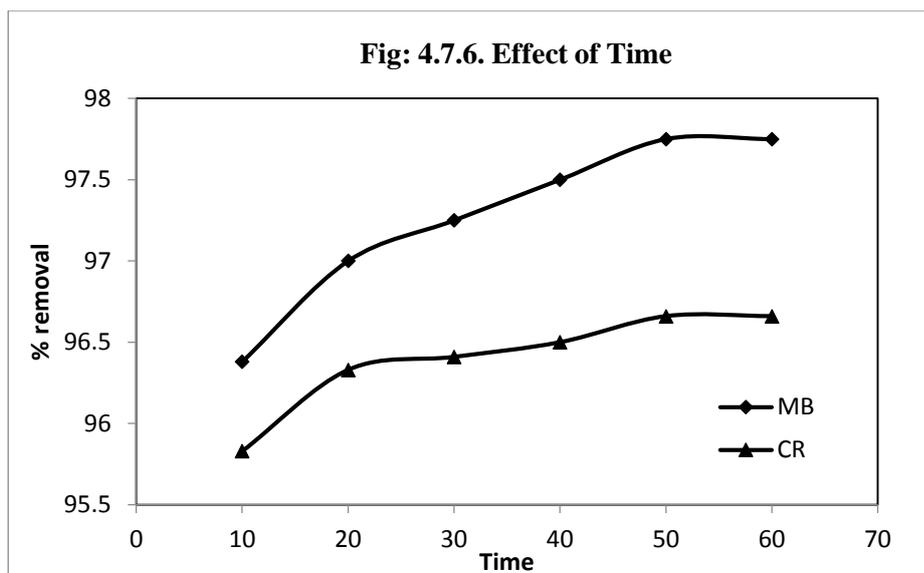
the surface area at higher concentration of the adsorbent. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption.



This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles. From the results, it is revealed that within a certain range of initial dye concentration, the percentage of dye adsorption on mango leaf powder is determined by the sorption capacity of the powder. The maximum removal of dye was obtained in the adsorbent dose of 80mg.

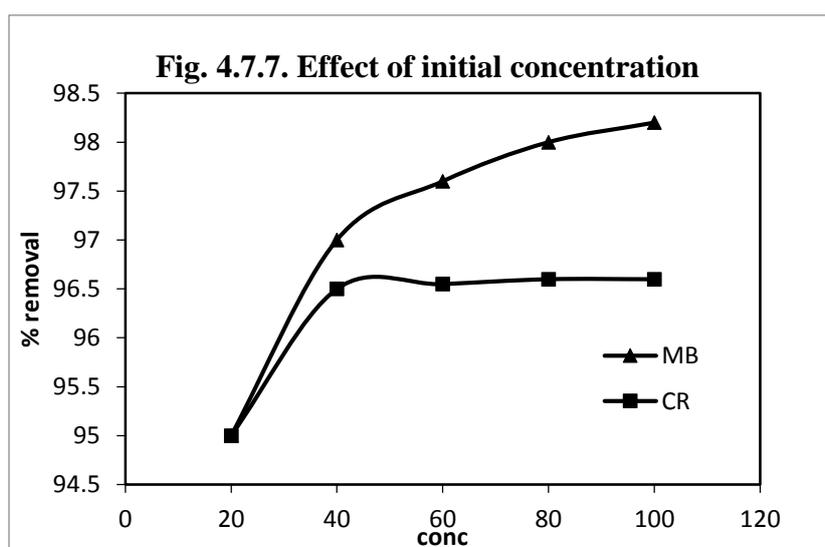
4.7.3. Effect of contact time

Adsorption of dyes was measured at different contact time for two different dyes. Fig.4.7.6, reveals that the rate of percent of dye removal is higher at the beginning. This is probably due to larger surface area of the leaves being available at beginning for the adsorption of dyes ions. Most of the maximum percent dye removal was attained after about 60 min of shaking time for different initial concentrations. The increasing contact time increased the dye adsorption and it remains constant after equilibrium reached in 50 min.



4.7.4. Effect of initial concentration

The effect of initial dye concentration in the range of 20 to 100 ppm on adsorption is shown in Fig. 4.7.7. It is seen that the removal of dye was dependent on the concentration of dye as the increase in the initial concentration increased the amount of dye removed up to 40 ppm for methylene blue and Congo Red and then the % removal remains constant for Congo Red. In the case of methylene blue it goes on increasing with the increase in initial concentration. The results indicate that the absorption of methylene blue is more by mango leaf powder.

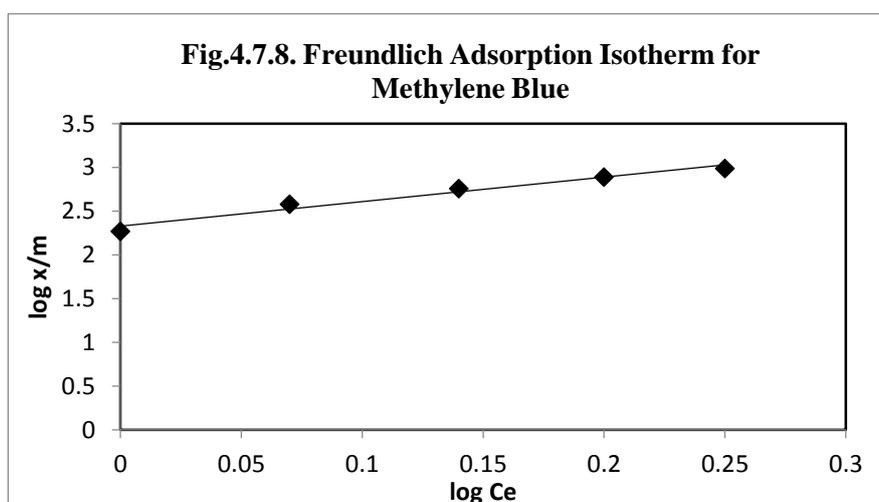


4.7.5. Isotherm data analysis

The parameters obtained from the different isotherm models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid-phase concentration was tested with the Langmuir and Freundlich isotherm equations.

The Freundlich isotherm models are shown in Fig.4.7.7 and 4.7.8. Freundlich adsorption isotherm model was found to be suitable for adsorption of methylene blue and congo red on mango leaf powder. The applicability of the linear form of Freundlich adsorption isotherm was proved by the high correlation coefficients $R^2 > 0.91$. Correlation coefficient for Freundlich is higher compared to that of Langmuir in all the two cases.

The Freundlich constant, n also indicates the degree of favorability of adsorption. The value of K and n are obtained from the intercept and slope of the graph plotted between $\log x/m$ versus $\log C_e$. The values of n lies between 1 and 2 (Table.4.7.2), indicated that the adsorption is favourable with the Freundlich isotherm model. The similar results were earlier reported by the other investigators. Hence it should be noted that the Isotherm constants are important in understanding adsorption mechanism and their subsequent application for prediction of some important design parameters.



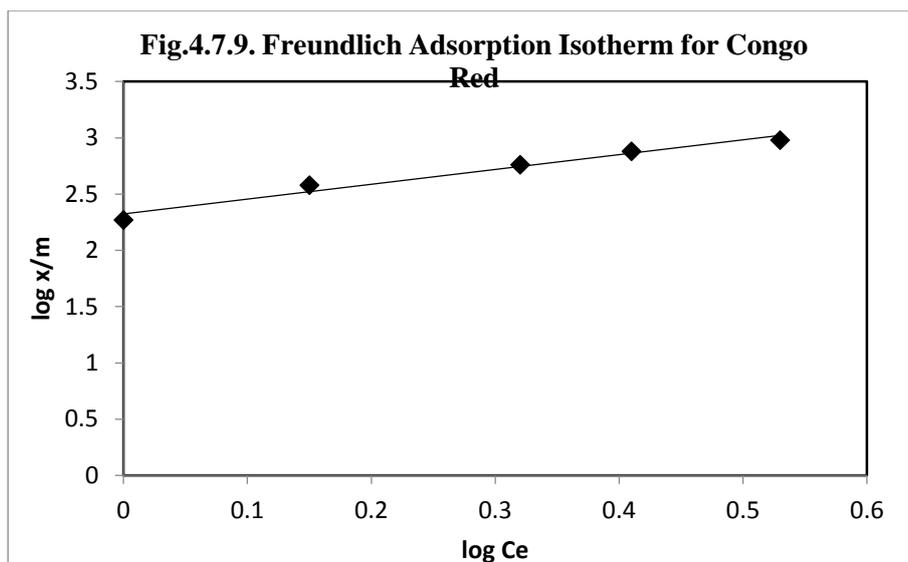


Table.4.7.2. Kinetic parameters for Freundlich isotherm

Dyes	Statistical Parameter Constant			
	R ²	K	n	r
Methylene Blue	0.978	212.324	2.8034	0.9872
Congo Red	0.972	210.377	1.3151	0.9853

4.7. 6. Kinetic models applied to the adsorption of dyes

The initial dye concentration of an effluent is important since a given mass of sorbent material can only adsorb a fixed amount of dye. The kinetics of dyes sorption was contact time dependent. Sorption increases with time and it remains constant after a contact time i.e. the equilibrium time. The response of the sorbent material used is not similar with all dyes used. The necessary time to reach equilibrium is in the range of 50min and, an increase of sorption time did not show notable effects. A possible explanation for the difference in sorption of the dyes can be given on the basis of their molecular weight and structural complexity. According Desai et al., the sorption kinetics and equilibrium are dependent upon the molecular dimensions of dyes.

For an appropriate description of the mechanism of dye sorption, it was necessary that different kinetic models be tested to determine their extent of fitness to the experimental sorption data. Thus, the kinetics of MB and CR adsorption onto mango leaf powder were analyzed using pseudo-first-order and pseudo second-order kinetic models. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R^2 , values close or equal to 1). The relatively higher value is the more applicable model to the kinetics of dye adsorption onto mango leaf powder.

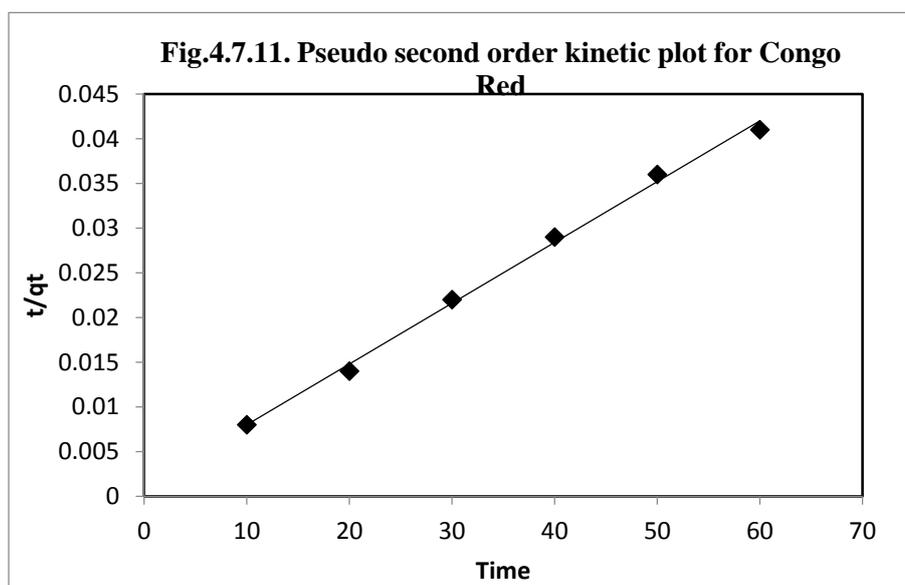
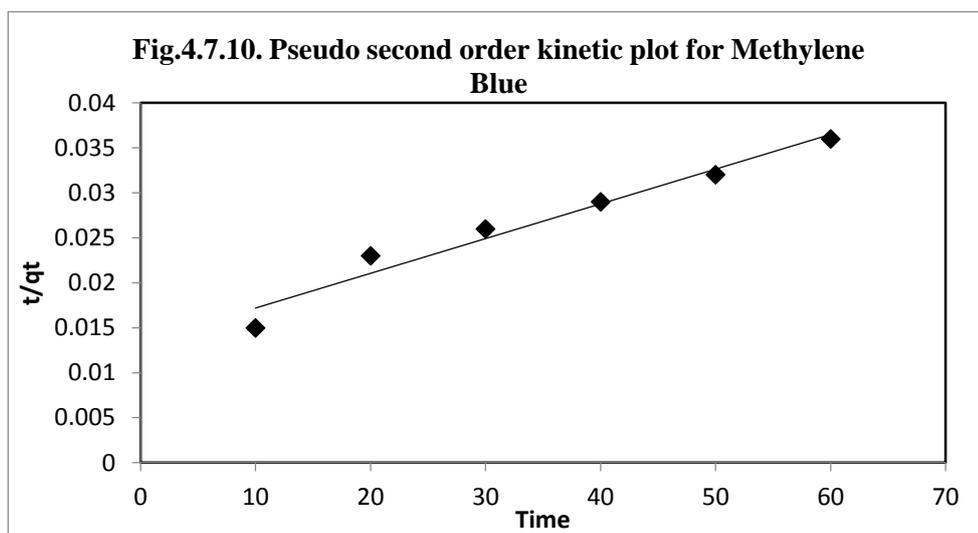


Table 4.7.3.presents the values of the linear coefficient of determination (R^2) values of the different kinetic models used to evaluate the sorption of dyes onto the mango leaf powder. Examination ofTable.4.7.3 shows that the pseudo-second order kinetic equation had the highest R^2 values. Thus this kinetic model was taken as the best fit equation for the description of the mechanism of sorption of dyes.

Table.4.7.3. Kinetic parameters for Pseudo-second order adsorption

Dyes	K	q_e	R²	r
Methylene Blue	1.2×10^{-5}	2500	0.9613	0.9804
Congo Red	4.0×10^{-4}	1428.57	0.9966	0.9982

In addition, examination of the sorption capacity values (q_e) of the pseudo second order model shows that the values were in the same range as the experimental sorption capacity values. Therefore, the sorption of dyes from aqueous solution onto the mango leaf powder adsorbents was found to follow the pseudo-second order kinetic equation. Furthermore, the pseudo-second order is based on the assumption that sorption follows asecond order mechanism, with chemisorption as the rate limiting step. So the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites.

4.8. Rice Husk as a Low Cost Adsorbent

4.8.1. Characterization of the adsorbent

a) FT-IR analysis

The IR spectral analysis is important to identify the characteristic functional groups on the surface of the adsorbent, which are responsible for adsorption of heavy metal ions. The IR spectrum of rice husk was recorded to obtain the information regarding the stretching vibrations of the functional groups which are involved in the adsorption of the adsorbate molecules. The IR spectrums of rice husk before and after metal ion adsorption are shown in the figure 4.8.1-3. The IR spectral analysis of rice husk shows distinct peak at 794.89, 1048.54, 1365.29, 1215.91, 1737.7 and 3332.65 cm^{-1} . The peak observed at 794.89and 1048.54 may be assigned to the presence of vinyl

compound ester group respectively. The peak observed at 1737.7cm^{-1} confirm the presence of carbonyl group. The peak at 3332.65cm^{-1} reveals $-\text{OH}$ group stretching. Also the band which can be seen at 1376.5 and is related to COO^- group.

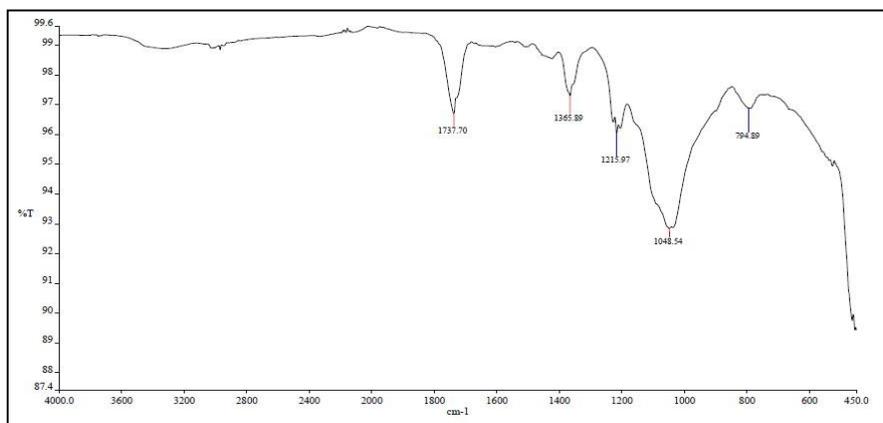


Fig 4.8.1. IR spectrum of rice husk

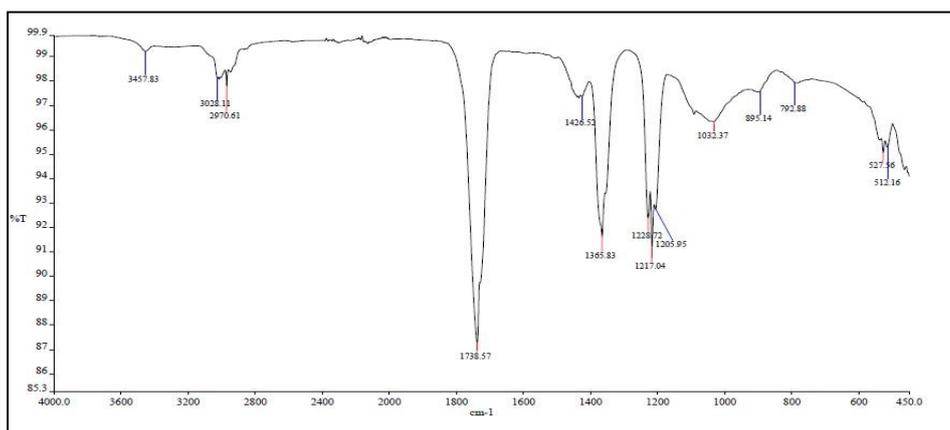


Fig.4.8.2. IR spectrum of rice husk loaded with Cr

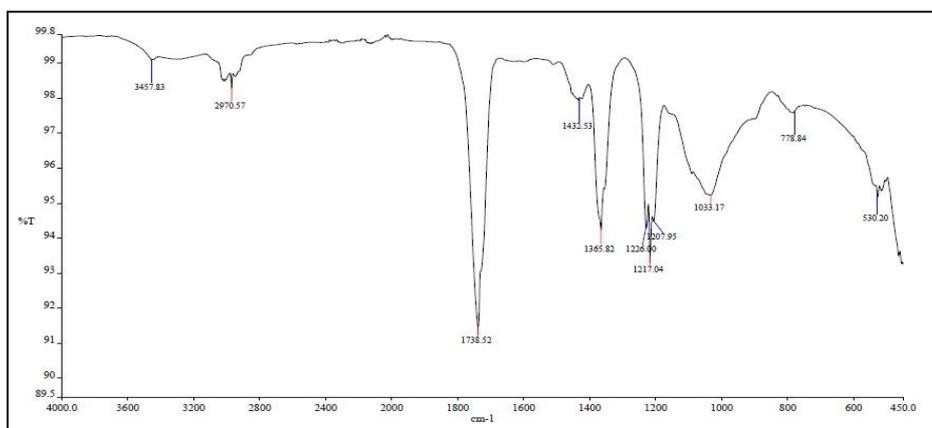


Fig.4.8.3. IR spectrum of rice husk loaded with Co

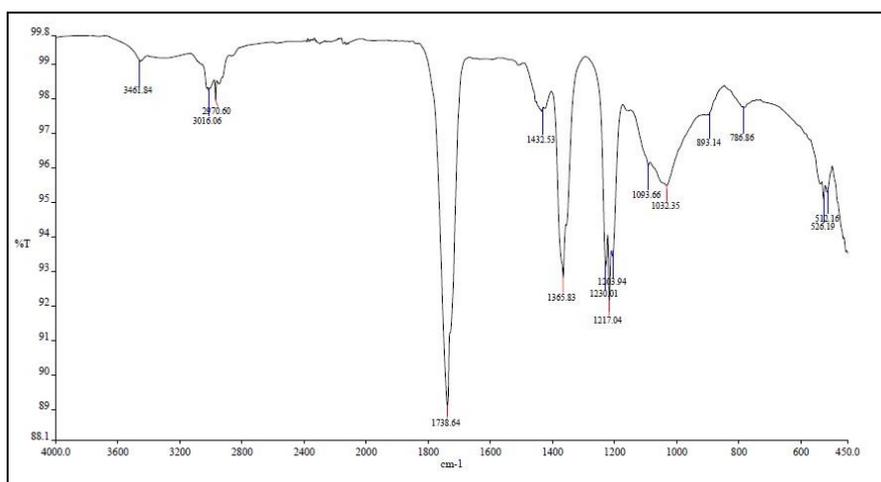


Fig.4.8.4. IR spectrum of rice husk loaded with Cu

b) SEM ANALYSIS OF THE SAMPLE

SEM analysis is another useful tool for the analysis of the surface morphology of an adsorbent. The porous and irregular surface structure of the adsorbent before adsorption can be clearly observed in SEM images shown in figure 4.8.5(a) &(b).

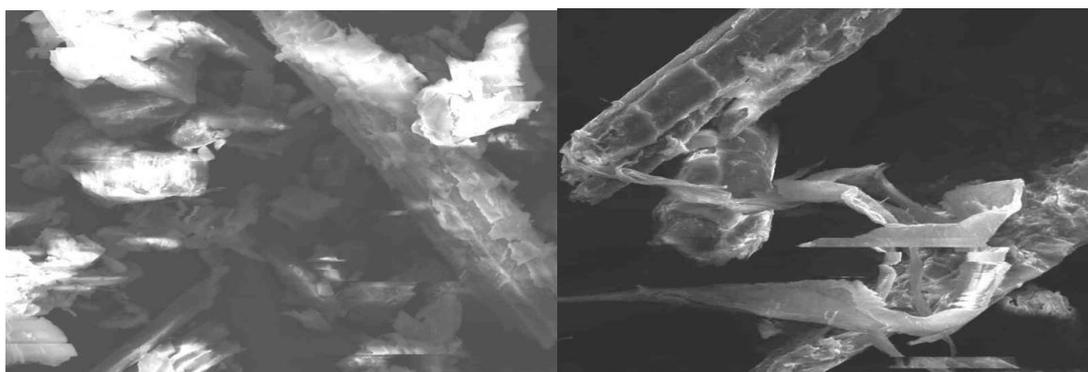
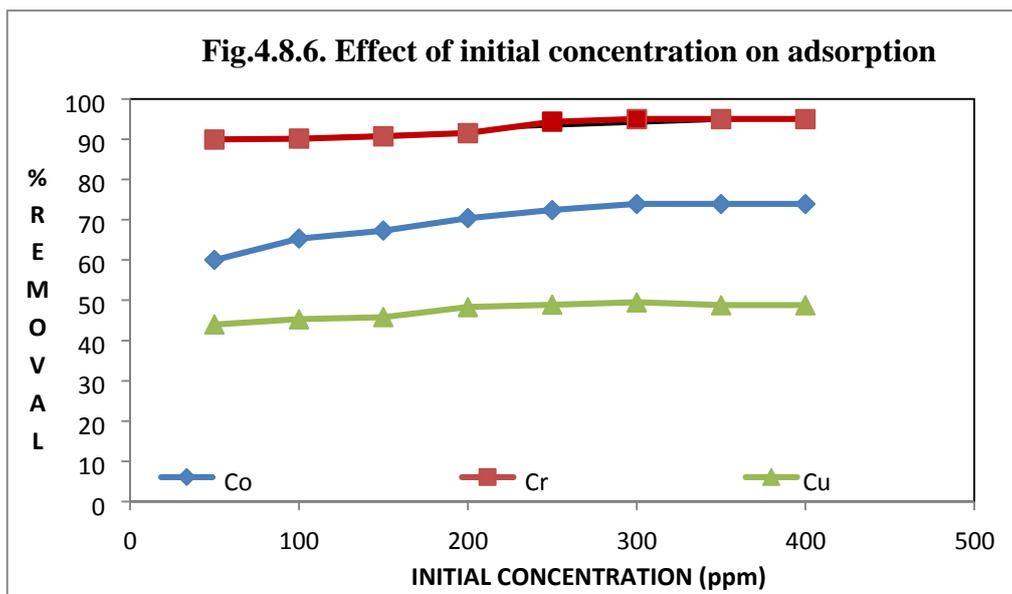


Fig.4.8.5. (a) SEM of rice husk (b) SEM of rice husk loaded with Chromium
The rough surface become smooth after metal ion adsorption (Fig.4.8.5.b)

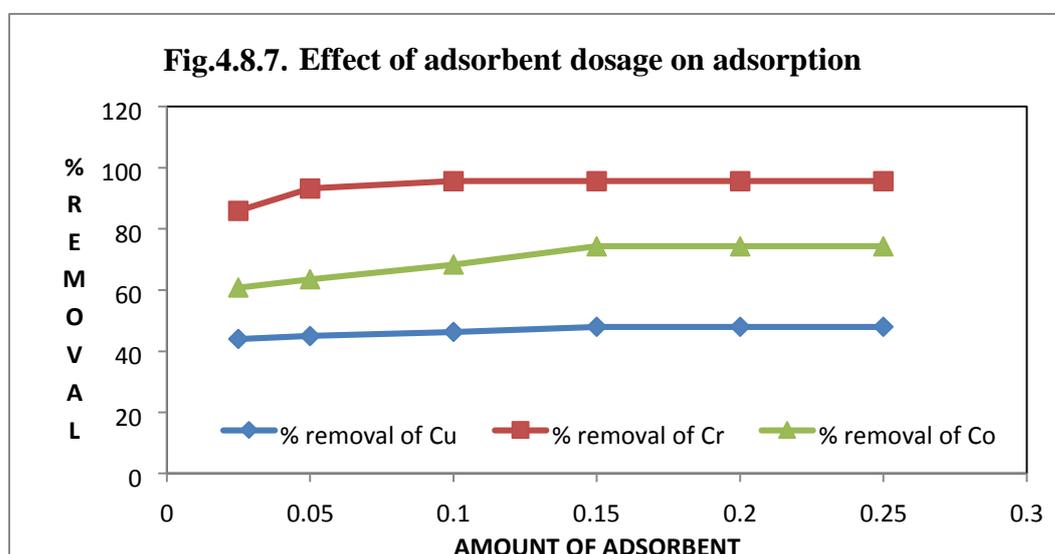
4.8.2. Effect of initial concentration

Initial metal ion concentration is one of the effective factors in removal efficiency. Fig.4.8.6. depicts the effect of increase in initial metal ion concentration on the adsorption of the various metal ions onto rice husk adsorbent. The strong affinities of Cu, Cr & Co on rice husk are indicated by the % removal of metal ions. The % removal is 95,48.8 & 73.9 for Cr, Cu and Co respectively.



4.8.3. Effect of adsorbent dosage

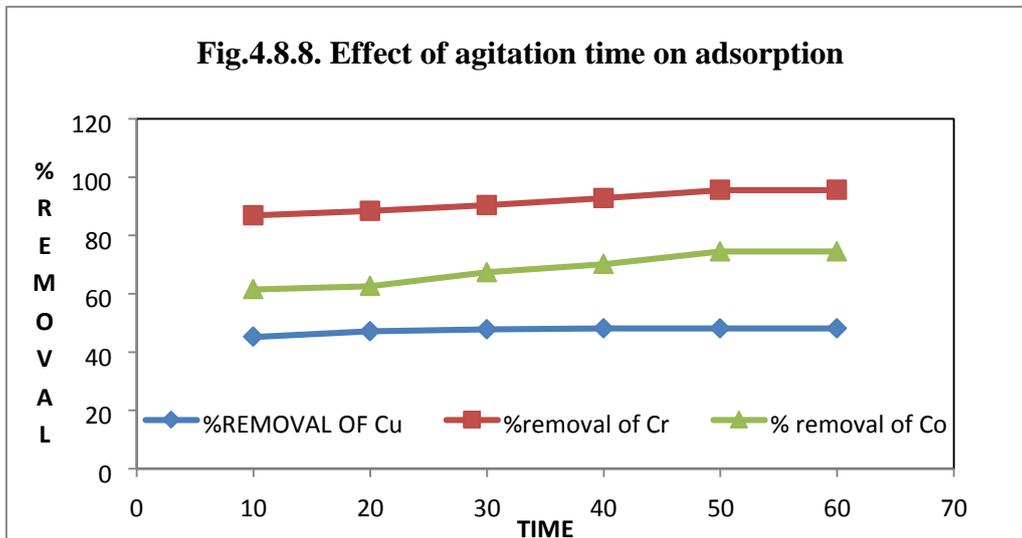
The effect of adsorbent dosage is illustrated in figure 4.8.7. It was found that the percentage of metal ion removal was increased as the adsorbent dosage increased from 50mg to 300mg. This is because increase in adsorbent dosage attributed to increase in surface area and availability of more adsorption sites.



4.8.4. Effect of agitation time

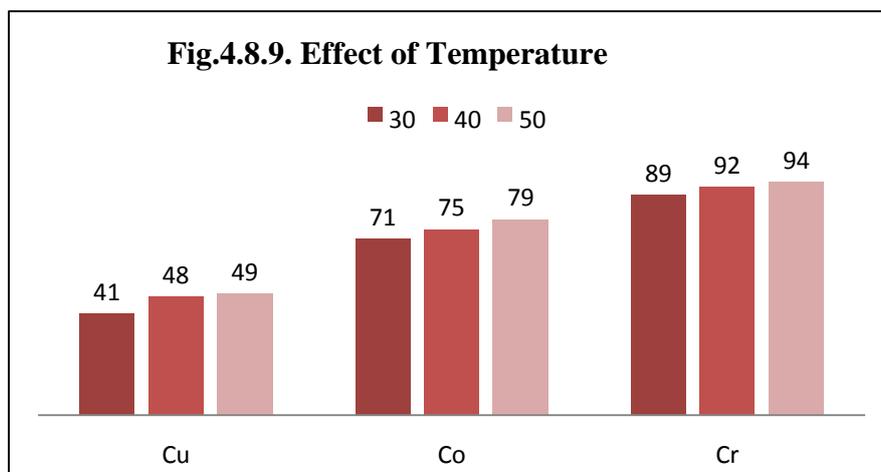
To establish an appropriate contact time between the rice husk and metallic ion solution, adsorption capacities of metal ion were measured as a function of time (Fig.4.8.8). The maximum adsorption percentage was 95.7%. This phenomenon may be related to the vacant adsorption sites on the adsorbent surface. During the initial stage

of sorption, a large number of vacant surface sites are available for adsorption. After lapse of time, the remaining vacant surface sites can be occupied difficultly due to repulsive forces between the solute molecules on the adsorbent surface and the bulk phase.



4.8.5. Effect of temperature

The results regarding the effect of temperature on the biosorption of metal ions by rice husk is shown in Fig.(4.8.9). The results indicated that, biosorption of metal ions increase with increase in temperature from 303-323K keeping other parameters constant.



The biosorption which is favorable at high temperature indicates the endothermic nature of the process. This might be due to the increase in the number of pores on the biomass surface at high temperature. The high temperature reduce the thickness of outer surface of rice husk and increase the kinetic energy of metal ions, as a result, the adsorption of the metal ions increases with temperature increases with temperature.

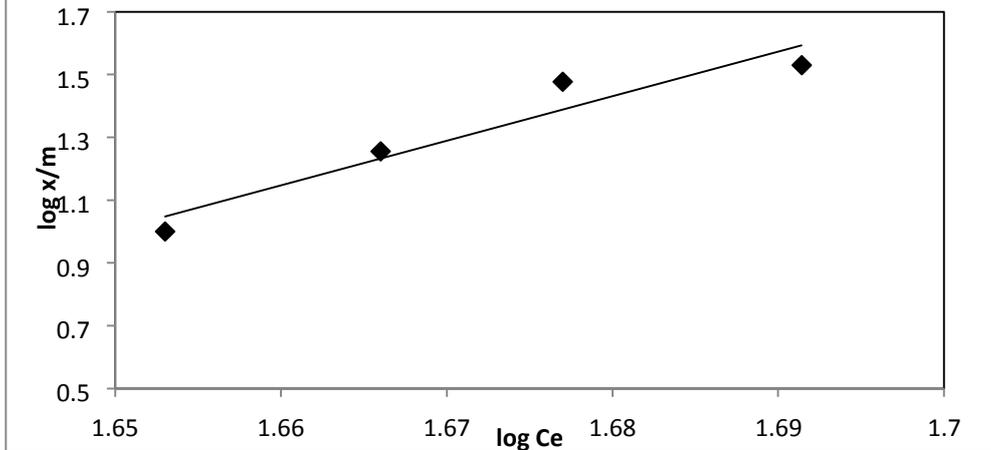
4.8.6. Isotherm data analysis

Adsorption isotherms described the adsorption process and the interaction between adsorbates and adsorbents. It is important to establish the most acceptable correlations for the batch equilibrium data for analysis and design of adsorption systems. The Langmuir and Freundlich models are the most frequently used to describe the equilibrium data of adsorption. In the present work, these two models were applied on the study of adsorption isotherms of metal ions.

Taking into consideration the values of the coefficient of correlation as criteria for goodness of fit, for most investigated systems the Freundlich equation gives a better correlation between the theoretical and experimental data for the whole concentration range when compared with Langmuir equations.

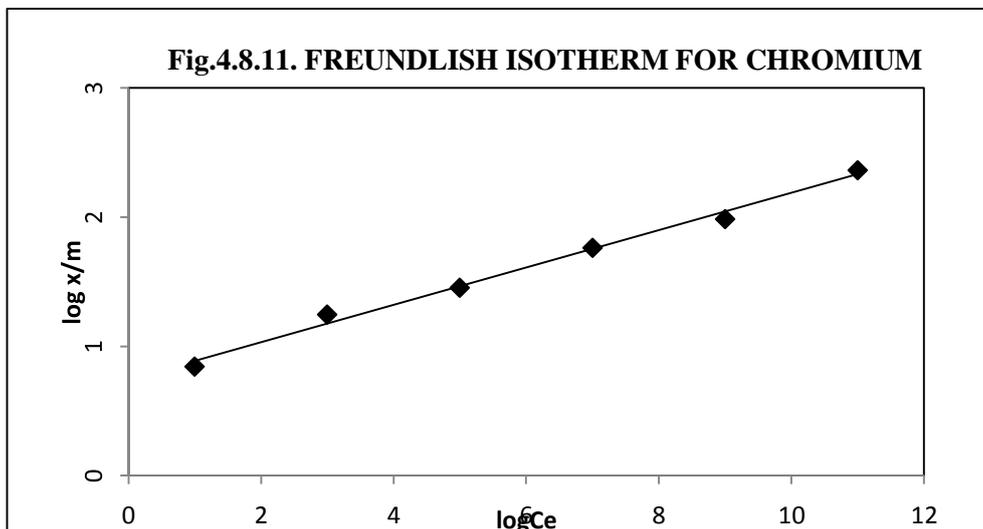
The Freundlich model assumes a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface, and the adsorption sites are distributed exponentially with respect to the heat of adsorption. Smaller value of implies stronger interaction between the adsorbent and heavy metal while equal to 1 indicates linear adsorption leading to identical adsorption energies for all sites. The parameters of Freundlich isotherm are shown in Table 4.8.1. Among the limited concentrations, the fact that the experimental data fitted well with the Freundlich isotherm model indicates that the surface of the adsorbent was nonuniform.

Fig.4.8.10. FREUNDLISH ISOTHERM OF COPPER



The Freundlich constant, n also indicates the degree of favorability of adsorption. The Freundlich constant, n have values lying in the range of 1 to 10 for classification as favorable adsorption. A smaller value of $(1/n)$ indicates a stronger bond between adsorbate and adsorbent while a higher value for k indicates rate of adsorbate removal is high. Hence it should be noted that the Isotherm constants are important in understanding the adsorption mechanism and their subsequent application for prediction of some important design parameters.

Fig.4.8.11. FREUNDLISH ISOTHERM FOR CHROMIUM



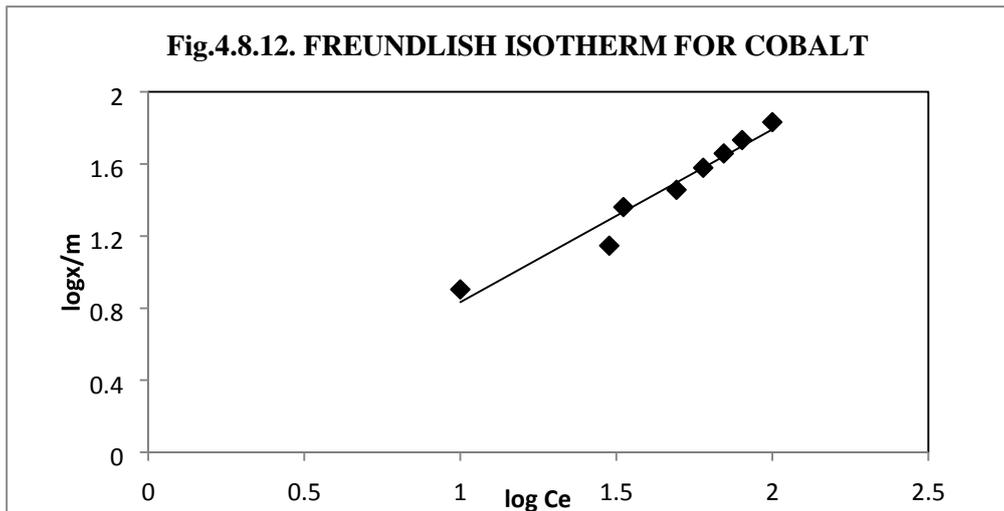
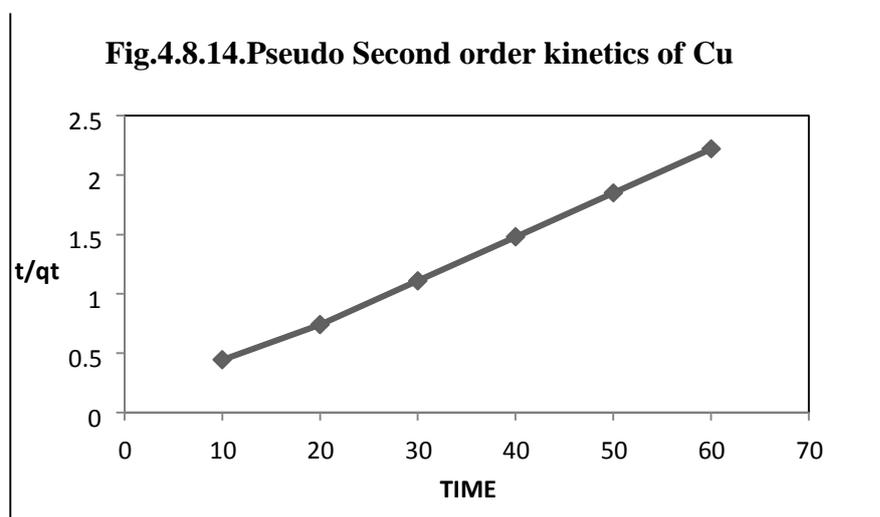
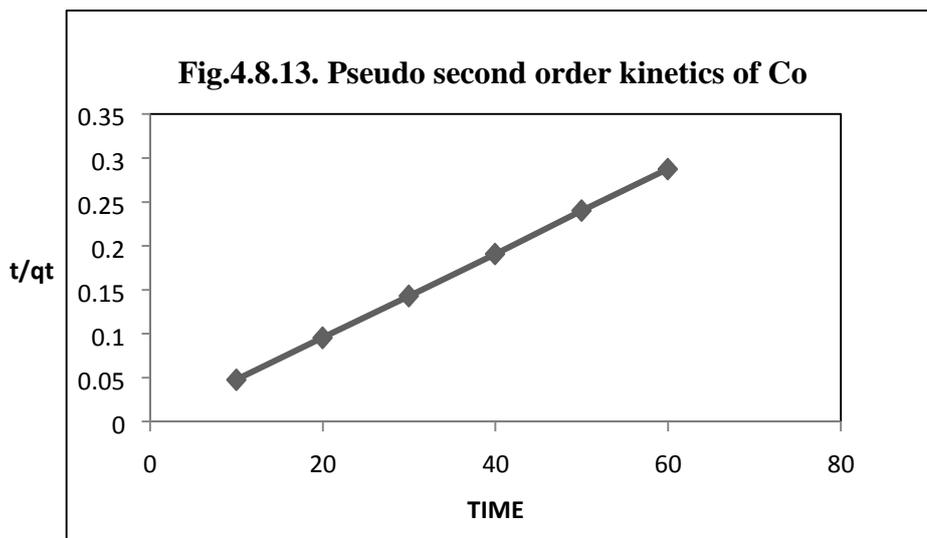


Table.4.8.1. Kinetic parameters for Freundlich isotherm

Metals	Statistical Parameter Constant			
	r	R2	K	n
Chromium	0.9893	0.9787	7.1187	2.8216
Cobalt	0.977	0.9545	4.8521	2.3821
Copper	0.9492	0.901	0.4267	1.5486

4.8.7. Adsorption kinetics

The kinetics of metal ion adsorption was evaluated by applying two common models: the pseudo-first-order kinetic model and the pseudo-second-order kinetic model. Several steps can be used to examine the controlling mechanism of adsorption process such as chemical reaction, diffusion control and mass transfer; kinetic models are used to test experimental data from the adsorption of Cu, Cr and Co. The kinetics of metal adsorption onto rice husk is required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes.



The pseudo-second-order model plots of Co, Cu and Cr adsorbed on rice husk were shown in figure 4.8.13-15 respectively. Comparing the correlation coefficient it could be detected that the kinetics of Cu, Cr and Co adsorbed on rice husk conformed to the Ho's pseudo-second order rate equation better than the Lagergren's pseudo-second order rate equation.

The pseudo-second-order kinetic model assumes that chemical adsorption can be the rate limiting stage involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate. The rate constant and correlation

coefficient can be calculated based on the plot of t/q_t versus t for metal ion adsorption.

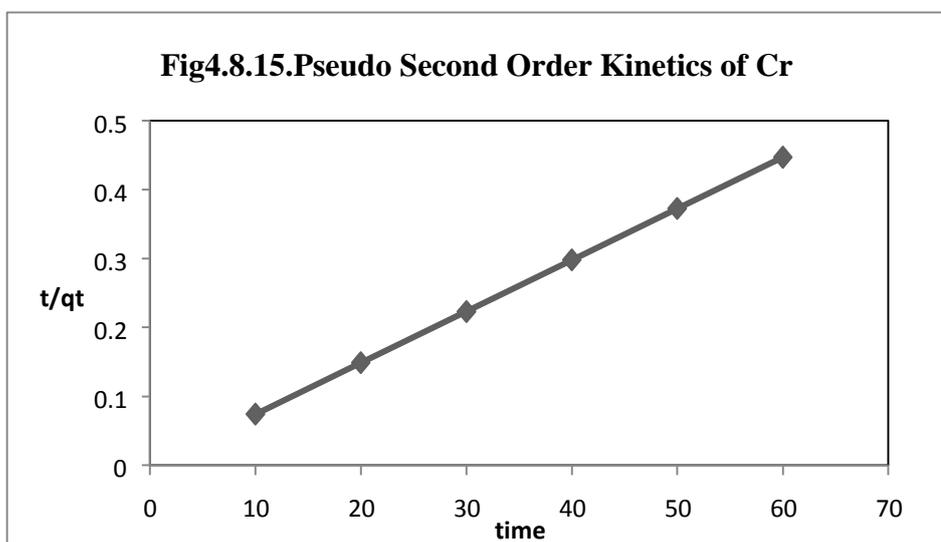


Table 4.8.2. The rate constant for Pseudo-second order adsorption

Metals	Statistical Parameter Constant			
	r	R ²	qe	Kad
Chromium	0.9899	0.9899	13.30	0.0345
Cobalt	0.9788	0.9788	9.18	0.0267
Copper	0.9160	0.9160	7.13	0.0253

4.9. Ground Nut Shell as Low Cost Adsorbent

4.9.1. Characterisation of the adsorbent

a) FT-IR spectroscopy

The IR spectral analysis is important to identify the characteristic functional groups on the surface of the adsorbent, which are responsible for adsorption of heavy metal ions. The IR spectrum of ground nut shell was recorded to obtain the information regarding the stretching vibrations of the functional groups which are involved in the adsorption of the adsorbate molecules. The IR spectrum of ground nutshell before and after metal ion adsorption is shown in the figure 4.9.1-4. The IR spectral analysis of ground nut shell shows distinct peak at 558.27, 1047.54, 1738.35 and 3335.08cm⁻¹. The peak observed at 558.2 and 1047.54 may be assigned to the presence of vinyl compound

ester group respectively. The peak observed at 1738.35cm^{-1} confirm the presence of carbonyl group. The peak at 3335.08cm^{-1} reveals OH stretching vibration. It can be seen from the spectra that upon adsorption of metal ions by ground nut shell, the broad OH and NH bands at 3395 cm^{-1} was shifted to 3285 cm^{-1} . This is indicative of the binding of metals with hydroxyl and amino groups. There is a shift in the C=O of ester from 1035 to 1031 cm^{-1} . This indicates that carboxyl groups are likely to be the main group to be involved in binding with metals. Since the biosorption was carried out at ambient pH which was higher than pH_{pzc} , the COOH groups will be deprotonated to form carboxylate ions which would attract the metal ions.

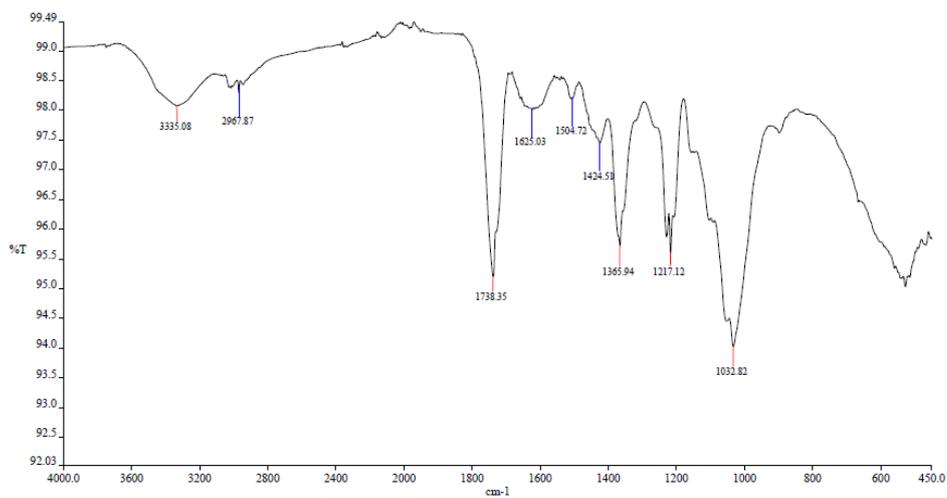


Fig 4.9.1. IR spectrum of ground nut shell

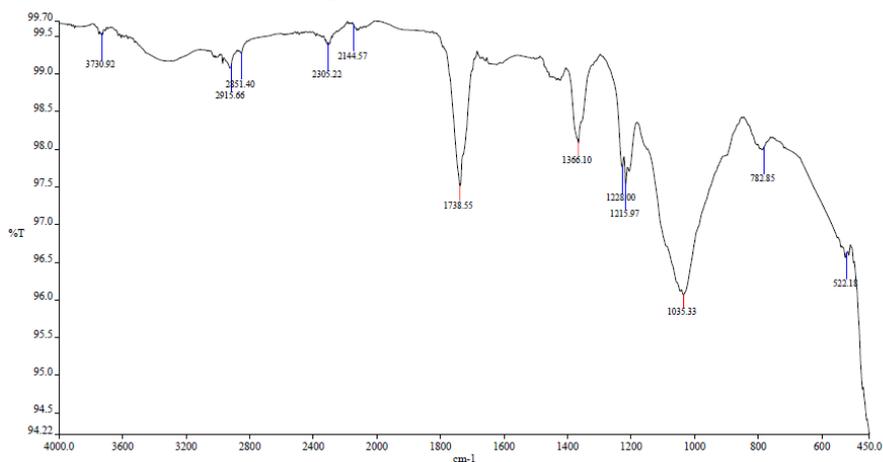


Fig.4.9.2. IR spectrum of ground nut shell loaded with Cr

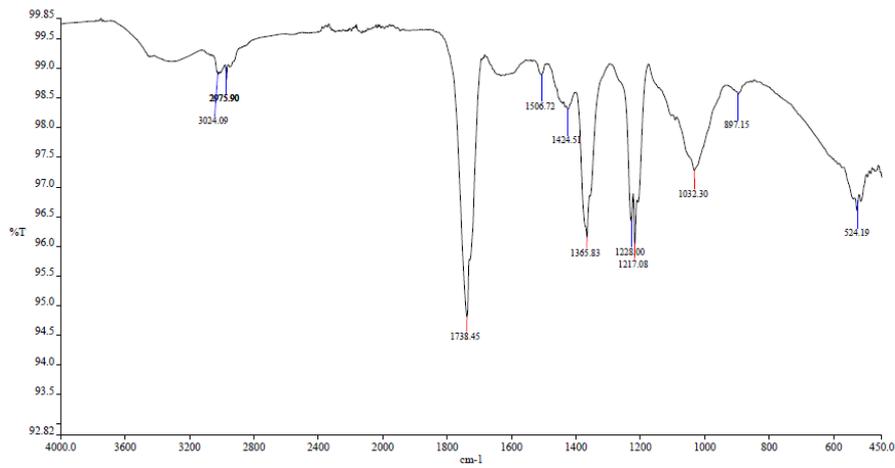


Fig.4.9.3. IR spectrum of ground nut shell loaded with Co

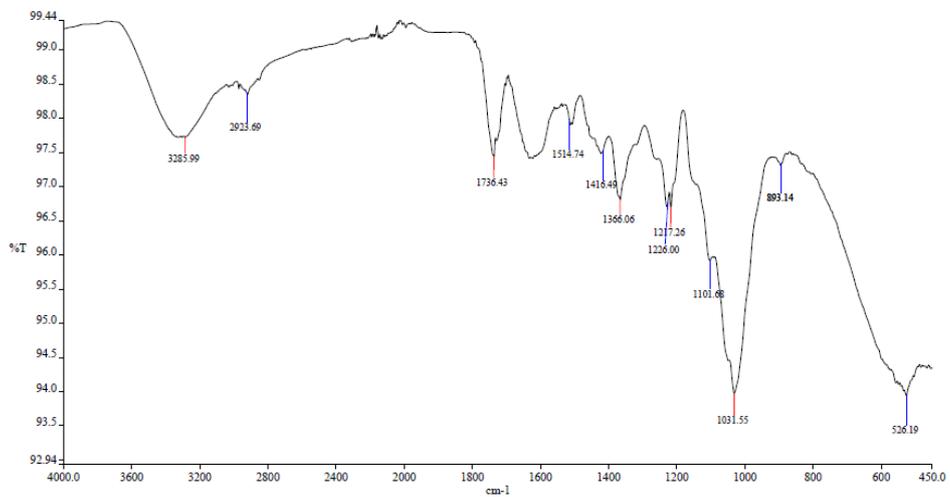


Fig.4.9.4. IR spectrum of ground nut shell loaded with Cu

b)SEM (Scanning Electron Microscope)

SEM studies stands for scanning electron microscopy, which is used for studying the surface morphology of substances due to its high magnification imaging capability.

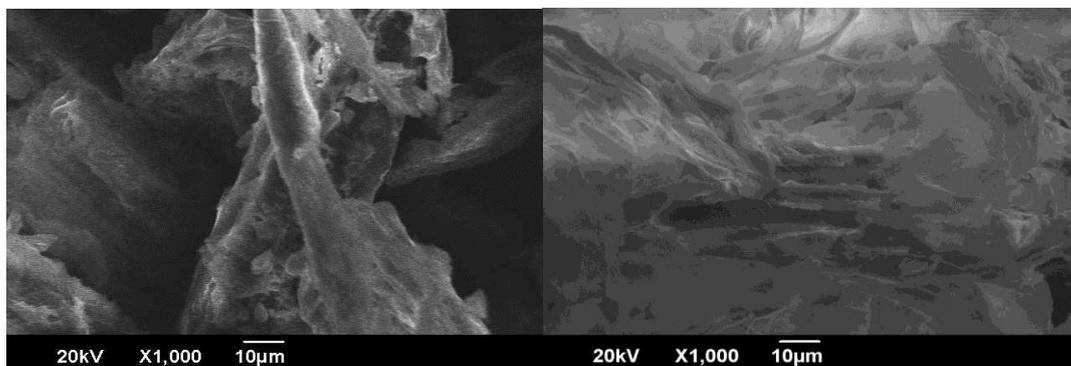
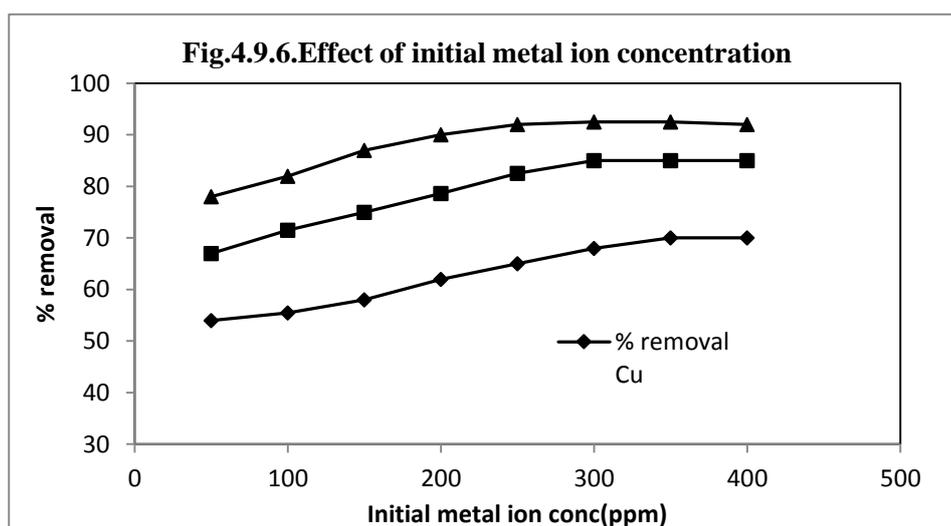


Fig. 4.9.5. SEM images of ground nut shell (a) before and (b) after adsorption

Scanning Electron Micrographs show the SEM images of ground nut shell before adsorption and after Cr (VI) adsorption. From fig. 4.9.5 (a) it can be seen that the ground nut shell surface consists of strands of fibres which are randomly arranged. Such arrangement could enhance the accessibility of the surface to the metal ions easily. Apart from these fibres, the surface is also very rough and uneven in nature, with pores and cavities and provides a large surface area for the adsorption of metals. This can be confirmed with fig. 4.9.5. (b) which shows that on treatment with metal, the surface roughness changed significantly and the pores are packed with metal ions after adsorption. The surface becomes smoother due to decrease in surface heterogeneity and adsorption of metal ions. Hence, it can be seen that both the fibrous and porous surface of ground nut shell could be the reason for its high adsorption capacity for metal ions as compared to most low-cost biosorbents reported.

4.9.2. Effect of initial concentration

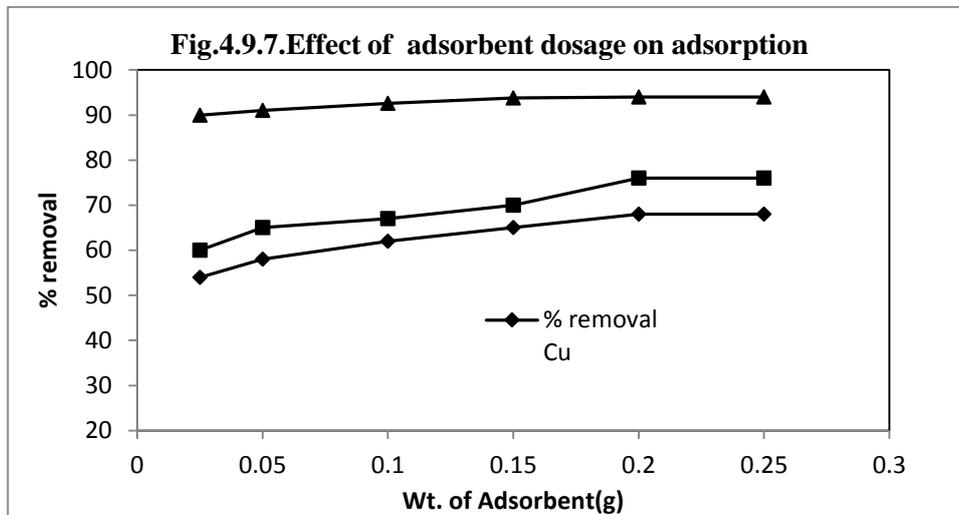
Initial metal ion concentration is one of the effective factors in removal efficiency. Fig.4.9.6 depicts the effect of increase in initial metal ion concentration on the adsorption of the various metal ions onto ground nut shell adsorbent. The strong affinities of Cu, Cr & Co the ground nut shell give concentration to a marginal variation in % adsorption with increase in initial metal ion.



4.9.3. Effect of adsorbent dosage

From the graph is apparent that by increasing the adsorbent dose the removal efficiency of each ion increases. This is readily understood from the fact that the number

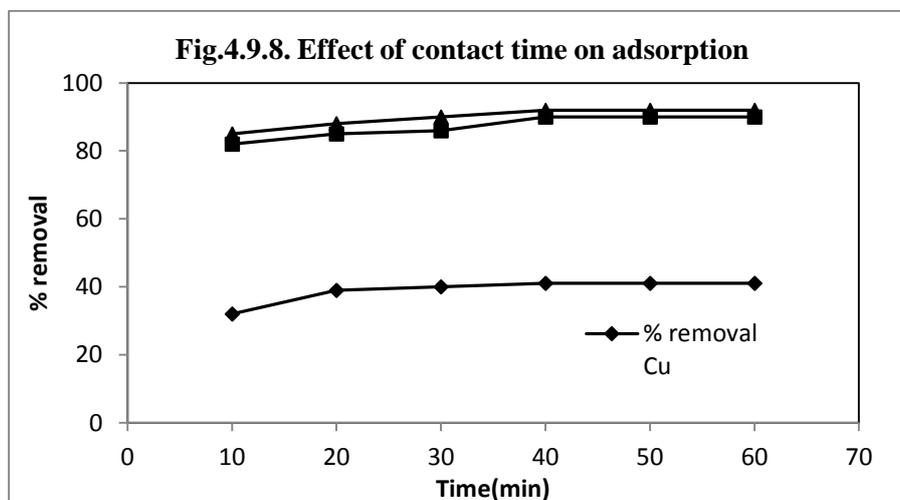
of available adsorption site increases by increasing the adsorbent dose and therefore, result in the increase in the removal efficiency or the % adsorption of the respective ion



Also, at a low adsorbent dose, e.g. 0.025g, the available sorption sites were quite insufficient compare with the large amount of adsorbate ions in the solution, resulting in low removal efficiency. However, at a higher adsorbent dose, e.g. 0.20g, the sorption sites were sufficient thereby resulting in a rapid removal of the different adsorbates. The adsorption order of the adsorbate on the ground nutshell was observed to follow the pattern Cr > Co > Cu.

4.9.4. Effect of agitation time

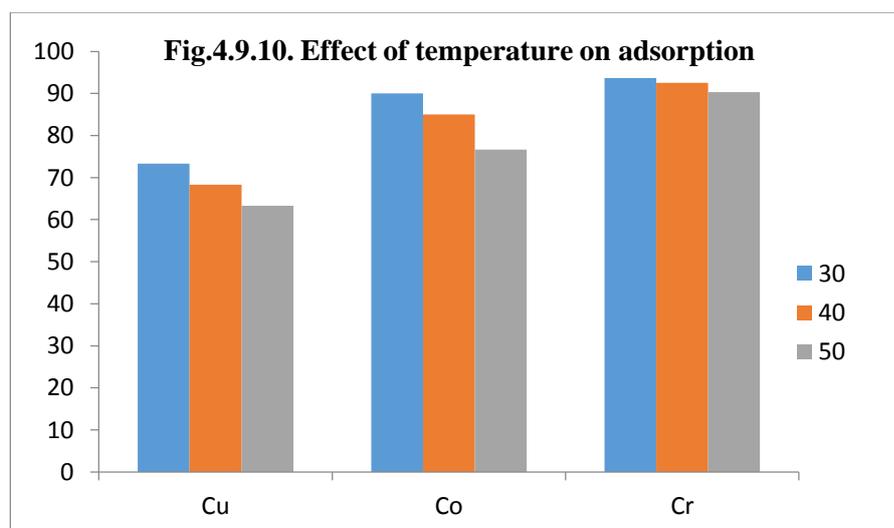
To establish an appropriate contact time between the ground nutshell and metallic ion solution, adsorption capacities of metal ion were measured as a function of time (Fig.4.9.8).



The plot reveals that the rate of the percentage of removal is higher at the beginning. That is probably due to the larger surface area of the ground nut shell being available at beginning for the adsorption of metals. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. The rate of metal ion removal was attained after approximately 40 min stirring.

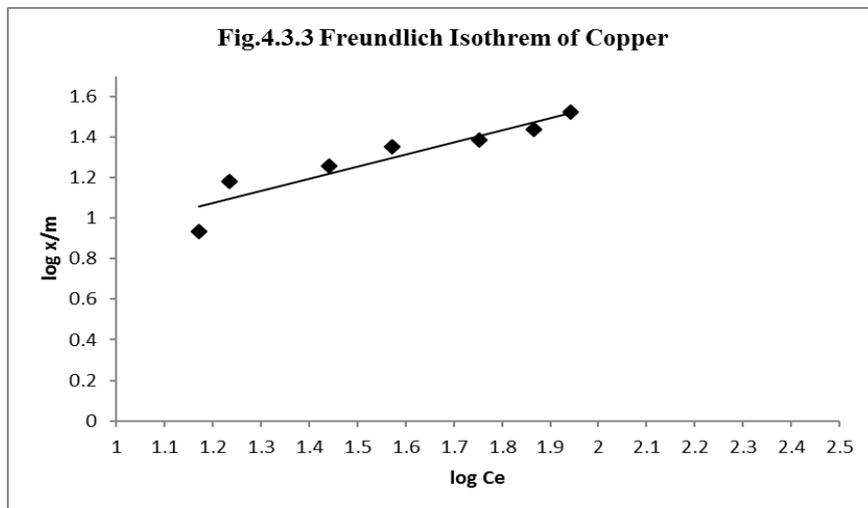
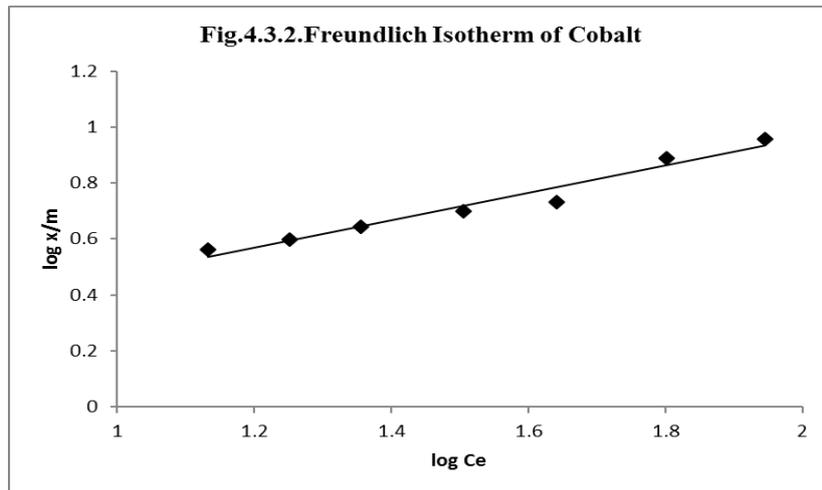
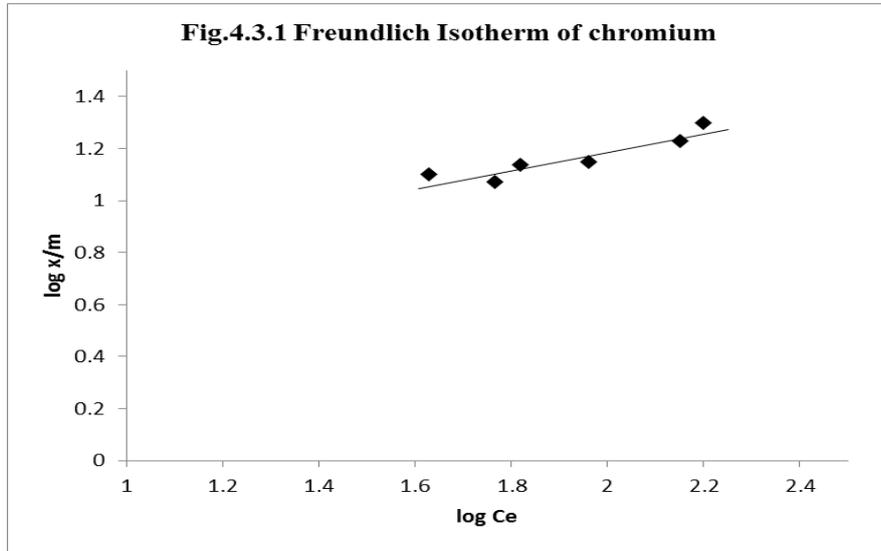
4.9.5. Effect of Temperature

Temperature dependence of the adsorption process is associated with several thermodynamic parameters. Fig.4.9.10 shows an decreasing trend of Cr (VI), Cu(II) and Co(II) removal with the rise in temperature from 30°C to 50°C. The decrease in metal ion uptake may be due to the exothermic nature of adsorption. As temperature increases adsorption decreases.



4.9.6. Isotherm data analysis

The parameters obtained from the different isotherm models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. Langmuir and Freundlich isotherms are used for fitting the experimental data in adsorption studies to understand the extent and degree of favorability of adsorption.



According to the obtained data for the model parameters it is obvious that Freundlich equilibrium model is favourable. Taking into consideration the values of the coefficient of correlation as criteria for goodness of fit, for most investigated systems the Freundlich equation gives a better correlation between the theoretical and experimental data for the whole concentration range when compared with Langmuir equations.

The Freundlich constant, n also indicates the degree of favorability of adsorption. The Freundlich constant, n have values lying in the range of 1 to 10 for classification as favorable adsorption. A smaller value of $(1/n)$ indicates a stronger bond between adsorbate and adsorbent while a higher value for k indicates rate of adsorbate removal is high. Hence it should be noted that the Isotherm constants are important in understanding the adsorption mechanism and their subsequent application for prediction of some important design parameters.

Table.4.9.1. Kinetic parameters for Freundlich isotherm

Metals	Statistical Parameter Constant			
	r	R²	K	n
Chromium	0.9913	0.9827	6.309	2.270
Cobalt	0.9802	0.9608	5.754	1.916
Copper	0.9079	0.8243	2.880	1.250

4.9.7. Adsorption Kinetics

Several steps can be used to examine the controlling mechanism of adsorption process such as chemical reaction, diffusion control and mass transfer; kinetic models are used to test experimental data from the adsorption of Cr, Cu onto Co. The kinetics of metal adsorption onto ground nut shell is required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes.

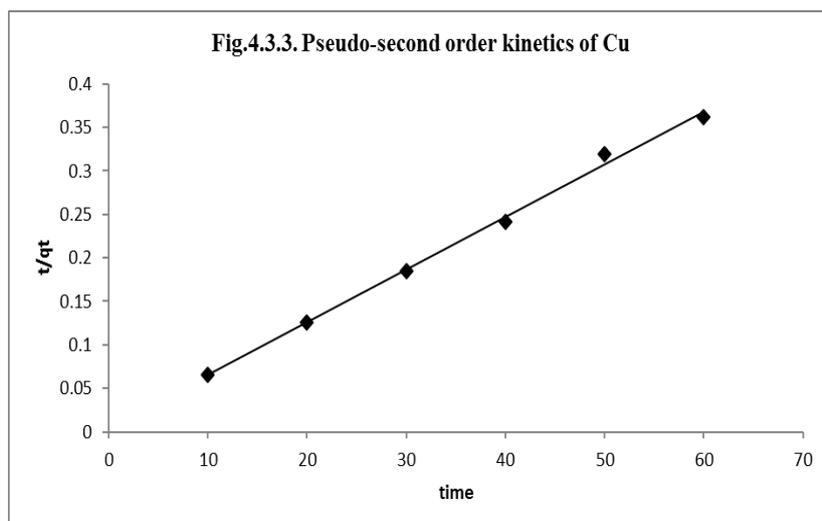
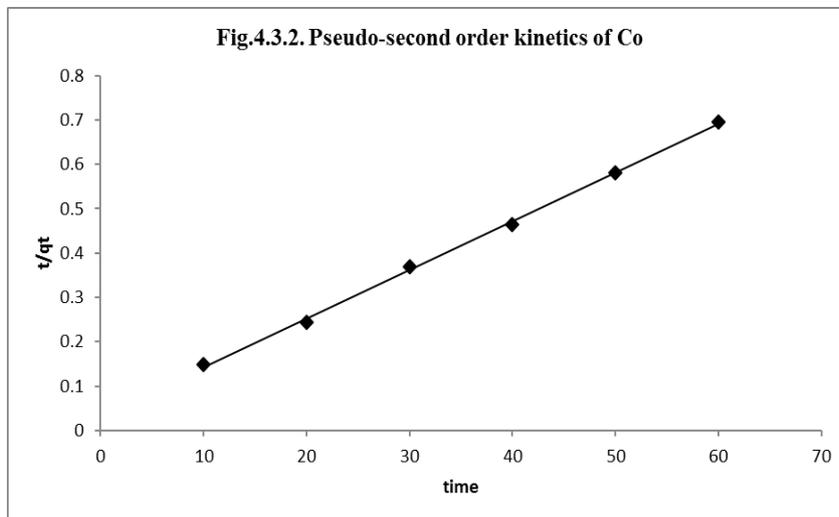
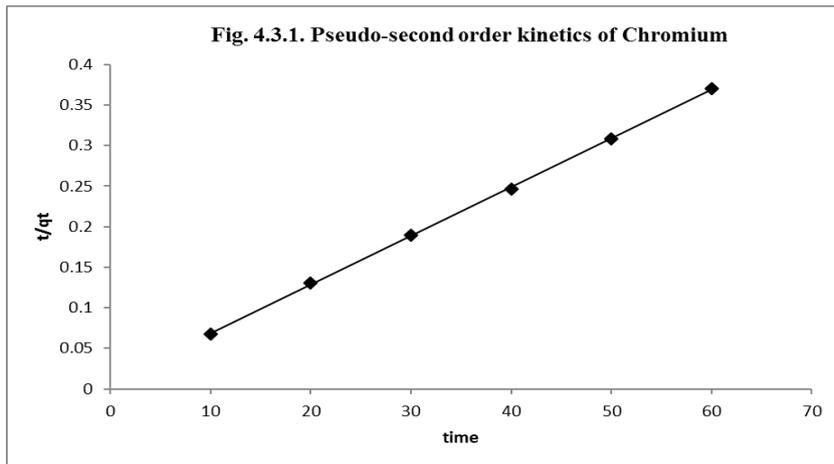


Table.4.9.2. Kinetic parameters for Pseudo-second order kinetics

Metals	Statistical Parameter Constant			
	R	R ²	K _{ad}	q _e
Chromium	0.9999	0.9998	0.1003	12.20
Cobalt	0.9996	0.9992	0.0139	8.22
Copper	0.9945	0.9890	0.0076	4.10

Table 4.9.2 presents the kinetic parameters resulted by fitting the pseudo-second order equation to the experimental data. The pseudo-second order model has been successfully used to fit the kinetic data. When the linearities of the plots of the two kinetic models were compared, the linearities of the chemisorptions pseudo-second order kinetic model were higher for each concentration than when the Lagrange pseudo-first order kinetic model was applied. This shows that the mechanism of the adsorption of metal ions by ground nut shell can be described by the pseudo-second order kinetic model, based on the assumption that the rate-limiting step may be chemisorptions involving valency forces through sharing or exchange of electrons between the hydrophilic edge sites of shell powder and metal ions. The correlation coefficient indicates that the kinetics of Cr, Co and Cu adsorbed on ground nut shell obey Ho's pseudo-second order rate equation.

4.10. Tamarind Shell as Low Cost Adsorbent

4.10.1. Characterisation of the adsorbent

a. FT-IR Spectroscopy

Infrared (IR) is the name given to the range in the electromagnetic spectrum between visible light and microwave radiation, conventionally from 0.8 μm to 1 mm wavelength ($12,500\text{--}10\text{ cm}^{-1}$). The far (1 mm–25 μm ; $10\text{--}400\text{ cm}^{-1}$) to mid-IR (25 μm –2.5 μm ; $400\text{--}4000\text{ cm}^{-1}$) range coincides with the energies needed to excite fundamental modes of rotation and vibration in gases, liquids or solids. The IR spectral analysis is important to identify the characteristic functional groups on the surface of the adsorbent, which are responsible for adsorption of heavy metal ions. The IR spectrum of tamarind shell was recorded to obtain the information regarding the stretching vibrations of the

functional groups which are involved in the adsorption of the adsorbate molecules. The IR spectrum of tamarind shell before and after metal ion adsorption are shown in the figure. The IR spectral analysis of tamarind shell shows distinct peak at 542.27, 1033.81, 1217.06, 1365.88, 1738.12, 2975.90, 3036.14, and 3449.79 cm^{-1} . The peak observed at 1033.81, 1217.06, 1365.88 cm^{-1} may be assigned to the presence of sulfoxide, aliphatic C-N vibrations, azides, aromatic nitro compounds respectively. The peak observed at 1738.12 cm^{-1} confirms the presence of carbonyl aldehyde group. The peak at 2975.90 reveals alkane stretching vibration, 3036.14 cm^{-1} for alkene and 3449.79 cm^{-1} for amine group respectively.

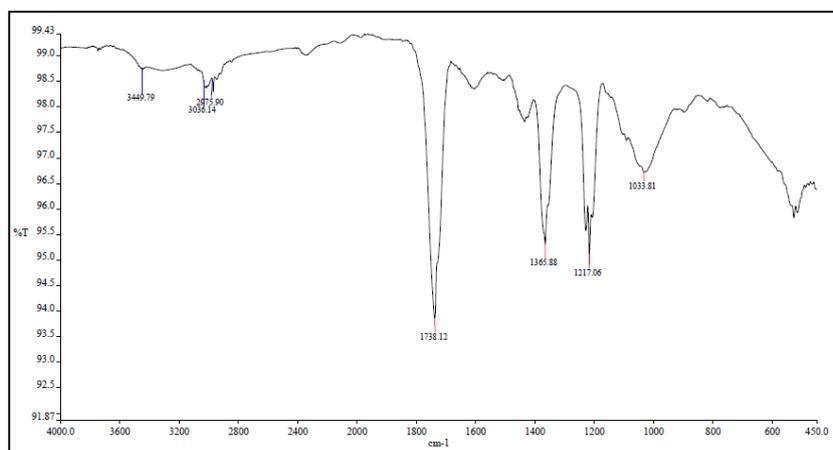


Fig.4.10.1. IR Spectrum of Tamarind Shell

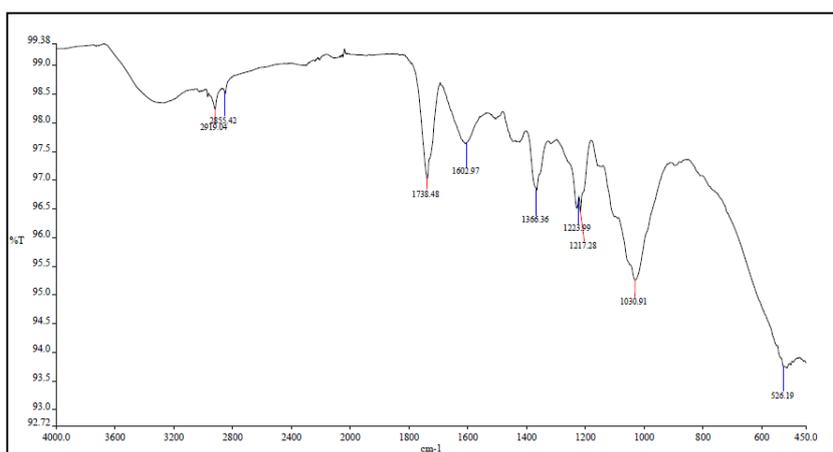


Fig.4.10.2. IR Spectrum of Tamarind Shell loaded with Cr

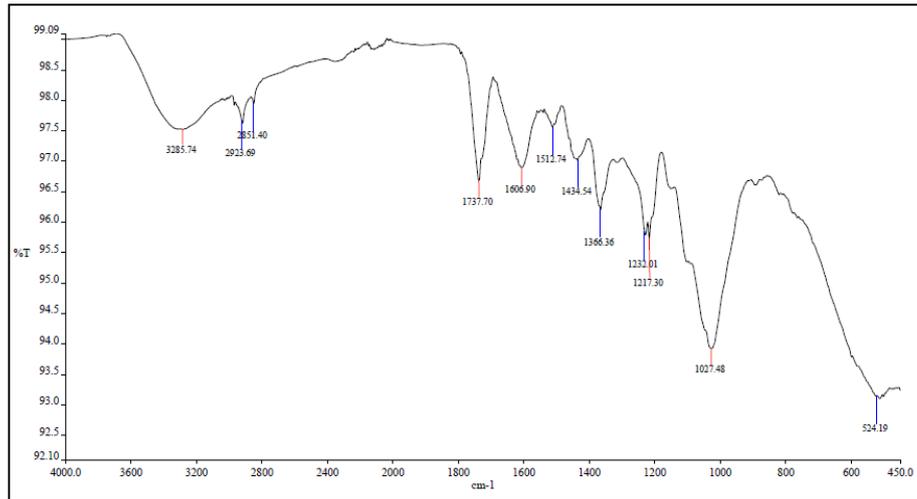


Fig.4.10.3. IR Spectrum of Tamarind Shell loaded with Co

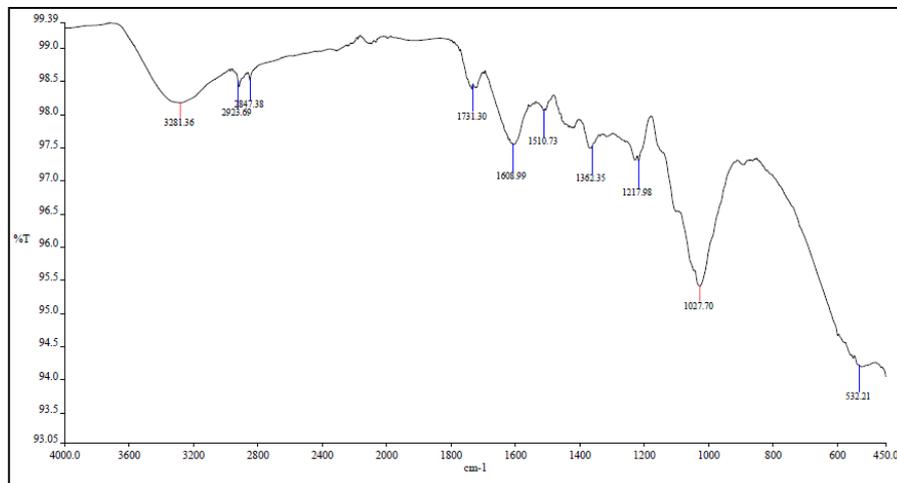


Fig.4.10.4. IR Spectrum of Tamarind Shell loaded with Cu

b) SEM Analysis

SEM analysis is another useful tool for the analysis of the surface morphology of an adsorbent.

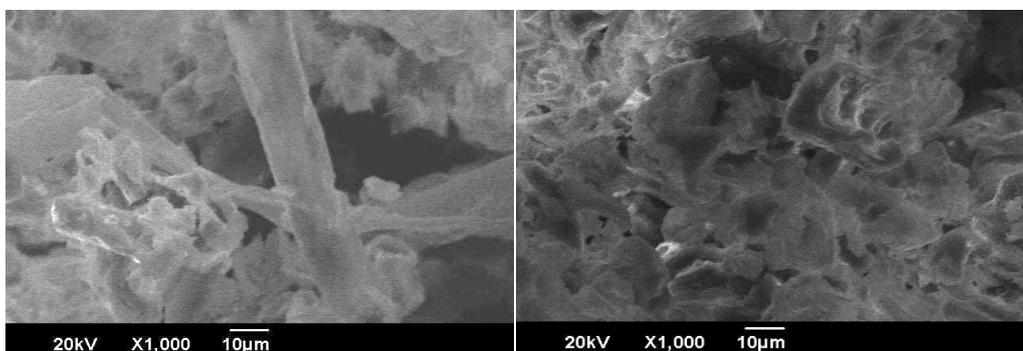
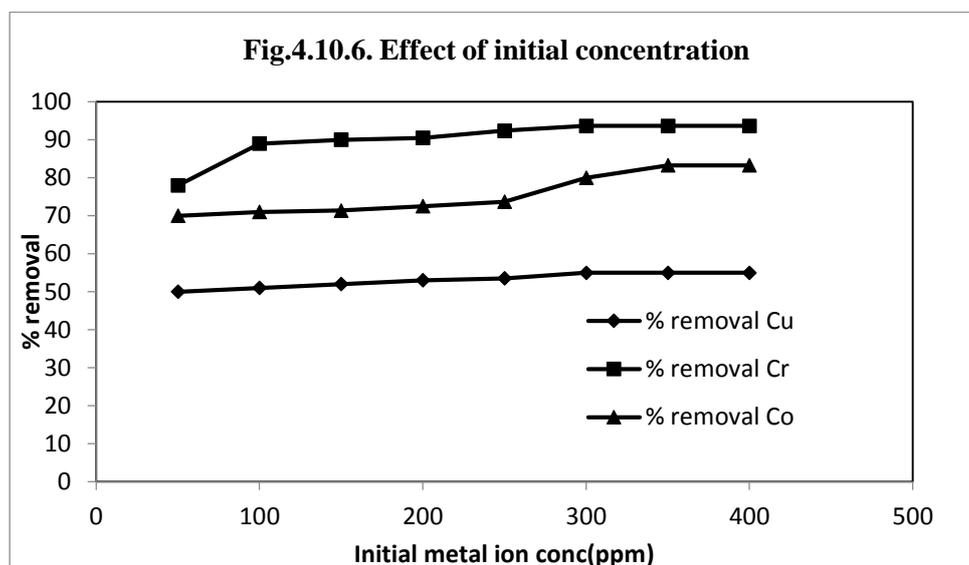


Fig. 4.10.5. SEM images of tamarind shell (a) before and (b) after adsorption

The porous and irregular surface structure of the adsorbent can be clearly observed in SEM images shown in Figure 4.10.5.b. It clearly reveals the porous surface textures which endorse the adsorbent with increased surface area and high adsorption capacity. The heterogeneous pores and cavities provided a larger exposed surface area for the adsorption of metal ions.

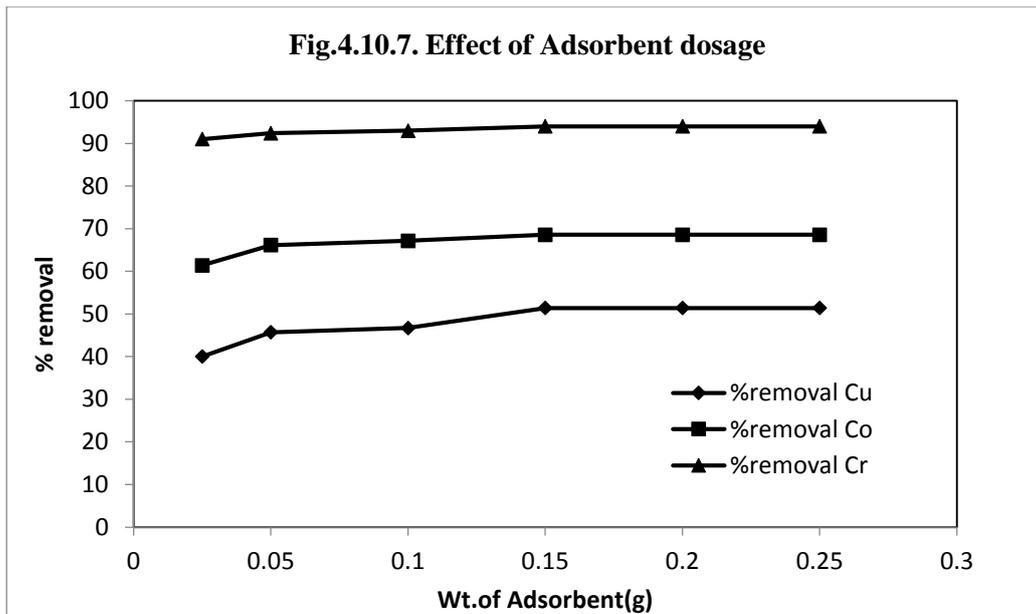
4.10.2. Effect of initial concentration

Initial metal ion concentration is one of the effective factors in removal efficiency. Fig.4.10.6 depicts the effect of increase in initial metal ion concentration on the adsorption of the various metal ions onto tamarind shell adsorbent. The strong affinities of Cu, Cr & Co to the tamarind shell give concentration to a marginal variation in % adsorption with increase in initial metal ion.



4.10.3. Effect of adsorbent dosage

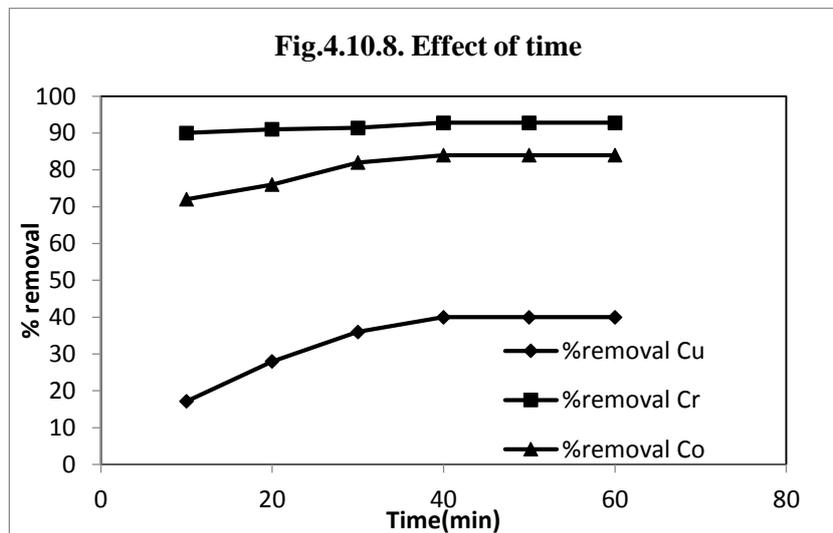
From fig.4.10.7, it is apparent that by increasing the adsorbent dose the removal efficiency of each ion increases. This is readily understood from the fact that the number of available adsorption site increases by increasing the adsorbent dose and therefore, result in the increase in the removal efficiency or the % adsorption of the respective ion. Also, at a low adsorbent dose, e.g. 2g, the available sorption site were quite insufficient compare with the large amount of adsorbate ions in the solution, resulting in low removal efficiency.



However, at a higher adsorbent dose, e.g. 0.25g, the sorption sites were sufficient thereby resulting in a rapid removal of the different adsorbates. The adsorption order of the adsorbate on the tamarind shell was observed to follow the pattern Cr > Co > Cu.

4.10.4 Effect of agitation time

To establish an appropriate contact time between the tamarind shell and metallic ion solution, adsorption capacities of metal ion were measured as a function of time (Fig.4.10.8).



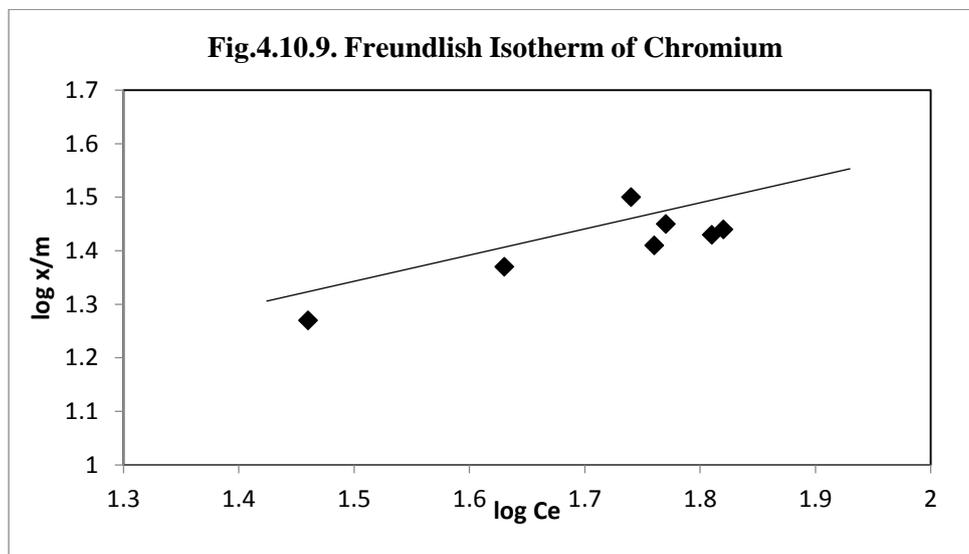
The plot reveals that the rate of the percentage of heavy metal ion removal is higher at the beginning. That is probably due to the larger surface area of the tamarind shell being available at beginning for the adsorption of metals. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is

transported from the exterior to the interior sites of the adsorbent particles. The rate of heavy metal ion removal was attained after approximately 50 min stirring.

4.10.5. Isotherm data analysis

The parameters obtained from the different isotherm models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. Langmuir and Freundlich isotherms are used for fitting the experimental data in adsorption studies to understand the extent and degree of favorability of adsorption. According to the obtained data for the model parameters it is obvious that Freundlich equilibrium model is favourable. Taking into consideration the values of the coefficient of correlation as criteria for goodness of fit, for most investigated Systems the Freundlich equation gives a better correlation between the theoretical and experimental data for the whole concentration range when compared with Langmuir equations.

The Freundlich constant, n also indicates the degree of favorability of adsorption. The Freundlich constant, n have values lying in the range of 1 to 10 for classification as favorable adsorption. A smaller value of $(1/n)$ indicates a stronger bond between adsorbate and adsorbent while a higher value for k indicates rate of adsorbate removal is high. Hence it should be noted that the Isotherm constants are important in understanding the adsorption mechanism and their subsequent application for prediction of some important design parameters.



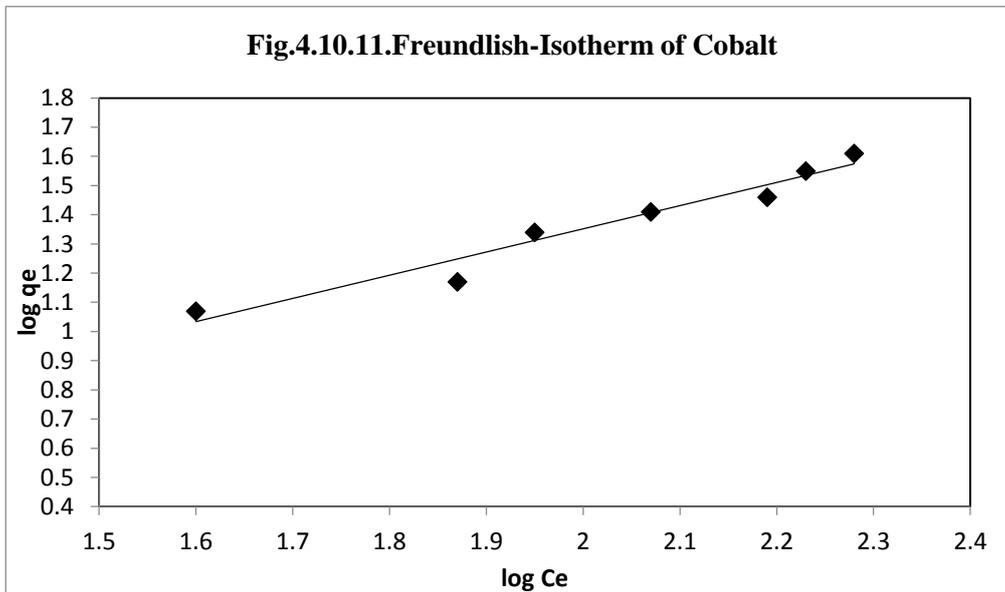
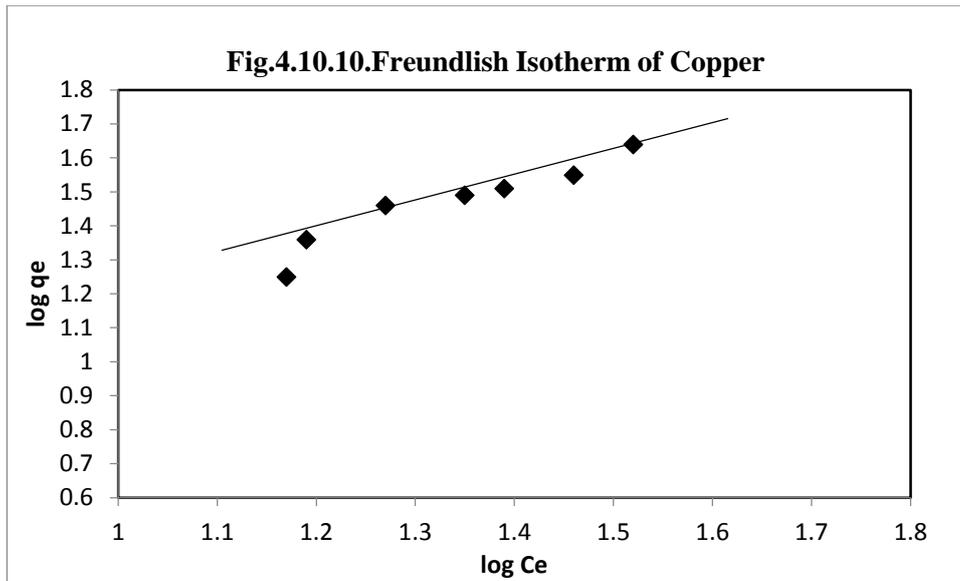
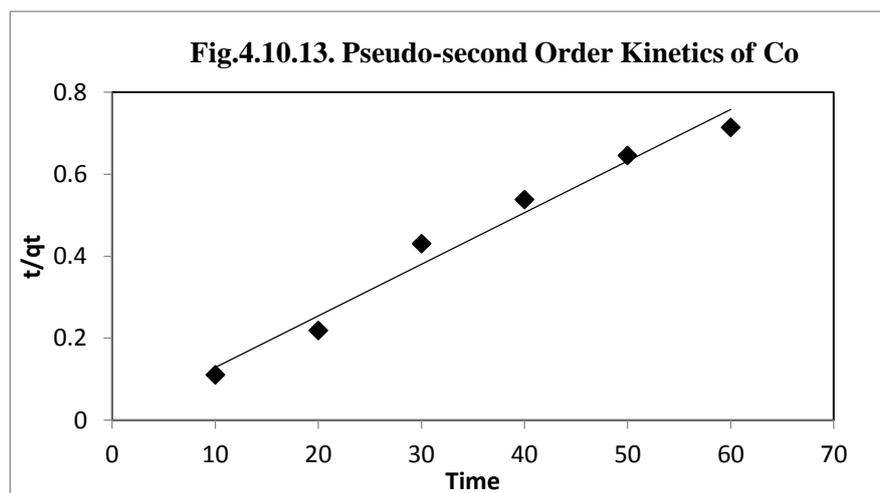
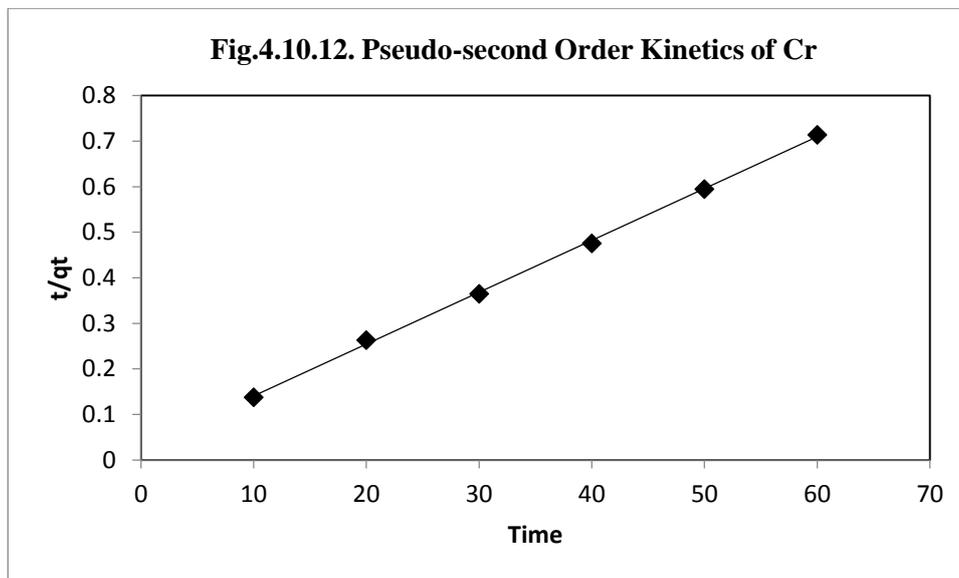


Table.4.10.1. Kinetic parameters for Freundlich isotherm

Metals	Statistical Parameter Constant			
	r	R ²	K	n
Chromium	0.9948	0.9896	19.9502	2.333
Cobalt	0.9794	0.9592	13.4896	2.083
Copper	0.9312	0.8671	7.9432	1.175

4.10.6. Adsorption kinetics

Several steps can be used to examine the controlling mechanism of adsorption process such as chemical reaction, diffusion control and mass transfer; kinetic models are used to test experimental data from the adsorption of Cr, Co onto Cu. The kinetics of metal adsorption onto tamarind shell is required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes.



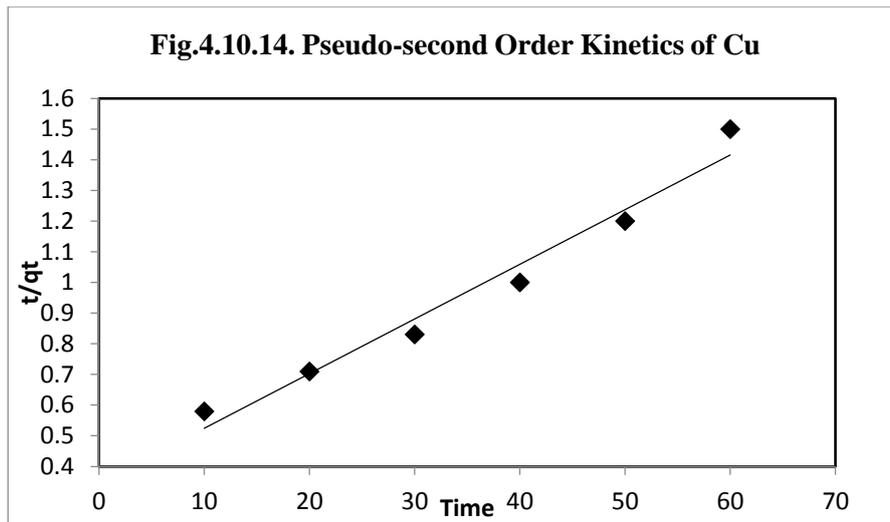


Table.4.10.2. The rate constant for Pseudo-second order adsorption

Metals	Statistical Parameter Constant			
	r	R ²	q _e	K _{ad}
Chromium	0.9997	0.9994	22.73	2.039
Cobalt	0.9945	0.9890	13.13	1.8502
Copper	0.9866	0.9734	9.42	0.9516

Chapter V

CONCLUSION

Adsorption was an effective process for decolorisation of textile waste waters. Although activated carbon was the most effective sorbent, other low cost sorbents could be used for color removal. The final choice of the sorbent is a matter of economics. Batch studies confirm that all the ten waste materials used as low cost adsorbent can be used as a substitute for high cost adsorbents.

Agricultural by-product waste pomegranate peel, potato peel, rice husk, saw dust, tamarind shell powder, ground nut shell, mango leaves, egg shell, used black tea and passionfruit peel were tested for the removal of cationic dyes, namely methylene blue, malachite green, eosin yellow, congo red and crystal violet and also for the removal of heavy metal ions. All the adsorbents were collected, washed with distilled water, dried, powdered and sieved. They were characterised by FT-IR spectroscopy and SEM.

Adsorption of dyes were studied on pome granate peel, potato peel, mango leaves, passion fruit peel, and used black tea as a function of amount of adsorbent, initial concentration of the adsorbate and agitation time. The adsorption capacity of pome granate peel decreased in the order crystal violet (CV) > malachite green (MG) > methylene blue (MB), the % adsorption is almost having the same range. i.e. 89-92.8%. The dyes sorption performances of potato peel are strongly affected by parameters such as contact time, adsorbant dosage and dyes type. About 97.8% removal was obtained for malachite green whereas the % removal was 96 and 92.4 for MB and CV respectively. The amount of dye sorbed by this material increased with the increase of these parameters at a specific time. The rate of adsorption increase with increase in initial dye concentration and decreased for MG and MV whereas it increased for CV.

The adsorption of dyes on passion fruit increased with the increase of initial concentration of dye, contact time and adsorbent dosage. The results of the investigation show that passion fruit peel has a suitable adsorption capacity for the removal of malachite green, crystal violet and eosin yellow from aqueous solution. The adsorption capacity of passion fruit peel decreased in the order Eosin yellow > Malachite green >

Crystal violet. About 94% removal was obtained for Eosin yellow whereas the percent removal was 75% and 70% for Malachite green and crystal violet respectively. With used black tea about 89% removal was obtained for malachite green, 73% for eosin yellow and crystal violet had a poor adsorption of 57.6%. The percentage removal of MG and EY increases with initial adsorbate concentration reaches a maximum and then decreases, whereas for CV, adsorption increases with dye concentration. Adsorption of all three dyes increases with the increase in adsorbent dosage and contact time. The possibility of adsorptive removal of dyes like methylene blue and Congo red from waste water by mango leaf powder has been examined. About 98% removal was obtained for methylene blue whereas the % removal was 96.5 for Congo red.

The egg shell could be employed as low cost adsorbents as alternatives to commercial activated carbon and other costly adsorbents for the removal of heavy metals from waste water over a wide range of concentrations. About 94.5% removal was obtained for chromium whereas the % removal was 85.1% and 73.5% for nickel and copper respectively. The rice husk has high potential for removal of heavy metals like Cu, Zn, Pb, Cd, Cr, Ni, Mn, Co, Fe, Hg and many more in terms of experimental conditions, high adsorption capacity, binding mechanisms and pre-treatment methods. The maximum sorption percentage was 95.8% for Cr(VI), 74.3% for Co(III) and 48.2% for Cu. The SEM image of rice husk showed that the rough structure of the sorbent surface could improve the adsorption capacity. The results of this study indicated that the uptake of Cu, Cr & Co ions by rice husk was affected by contact time, initial heavy metal ion concentration and agitation rate. The uptake of Cu, Cr & Co ions increased with increasing contact time and decreasing ions concentration and equilibrium was attained in 60 minutes of contact.

The study on ground nut shell as adsorbent has been successfully approved it to act as a potential low cost adsorbent for removal of heavy metals from aqueous solution as wastewater. About 94.8% removal was obtained for chromium whereas the % removal was 85 and 72% for Cobalt and Copper respectively. Tamarind shell act as a good adsorbent for heavy metal removal and the adsorption order of the adsorbate on the tamarind shell was observed to follow the pattern Cr > Co > Cu. The maximum sorption percentage was 93.66% for Cr(VI), 83.3% for Co(III) and 55% for Cu.

The results of the study on saw dust indicated that the uptake of Cu Ni & Co ions was affected by contact time, initial heavy metal ion concentration and agitation rate. The uptake of Cu Ni & Co ions increased with increasing contact time and decreasing ions concentration and equilibrium was attained in 60 minutes of contact. About 94.8% removal was obtained for chromium whereas the % removal was 85 and 72% for Cobalt and Copper respectively using Ground nut shell as the adsorbent.

From the kinetic model analysis using coefficient of determination, the pseudo-second order model was the most fitting for the description of dye transport from the bulk solution onto the surface of the mango leaf powder, pome granate peel, potato peel, used black tea powder and passion fruit peel.

The kinetic data obtained from the study using saw dust, ground nut shell, egg shell, rice husk and tamarind shell for the removal of heavy metal ions fitted well with the pseudo-second order model and the sorption profiles derived based on the pseudo-second order kinetic model showed good agreement with the experimental curves.

A good fitting of dyes sorption equilibrium data is obtained with Freundlich model in all the range of dyes concentrations studied for all the adsorbents, namely, mango leaf powder, pome granate peel, potato peel, used black tea powder and passion fruit peel. The equilibrium data conformed well to the Freundlich with a high correlation coefficient indicating that the adsorption of metal ions onto surface of the adsorbents followed a multilayer pattern.

The presents work is the study of employing ten different waste materials as low cost adsorbent for removal of cationic dyes like MB, MG, EY, CR and CV and heavy metals like Cr, Co Cu and Ni from water and waste water. Adsorbents prepared from domestic and agricultural waste, can successfully be used to remove the cationic dyes and heavy metals from an aqueous solution. The present study concludes that they could be employed as low-cost adsorbents as alternatives to commercial activated carbon and other costly adsorbents for the removal of dyes and heavy metals from wastewater over a wide range of concentrations. The adsorbents are inexpensive and readily available, thus this study provide a cost effective means for removing dyes and metal ions from contaminated water or effluents. The use of low cost adsorbents as potential bioadsorbent for metal remediation and dye removal and environment management

technologies has increased in recent past due to its easy availability, low cost, reusability, high efficiency, easy processing, application and recovery without any adverse impact on the environment.

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