



## REMOVAL OF HEAVY METAL FROM INDUSTRIAL WASTE WATER BY USING BANANA PEEL AS BIOADSORBENT

**Manisha Priyadarshini Tripathy** , tripathypmanisha@gmail.com

**Umakanta Pradhan** , Assistant Professor , AIET, Bhubaneswar, umakanta.pradhan@aryan.ac.in

### ABSTRACT:

Pollution of heavy metal ions in the environment is a critical problem because of their toxicity and other adverse effects on water and soil. The heavy metals must be removed from wastewater before discharging them into water bodies. Heavy metal chromium can often be found in industrial wastewater and their discharge to the environment poses a serious threat due to their acute toxicity to aquatic and terrestrial life which also includes humans. The presence of highly toxic and carcinogenic hexavalent chromium (Cr(VI)) in effluent streams is a major environmental issue. The effluents of electroplating, tannery and metal finishing industries etc. are the major source for the Cr(VI) production in wastewater streams. Different techniques are used for the removal of heavy metals from wastewater i.e., reverse osmosis, electrochemical treatment, evaporative recovery, ion exchange, chemical precipitation, membrane filtration and adsorption by activated carbon. All these methods are expensive. The present work deals with determination of Cr(VI) removal capacity from synthetically prepared waste water by using banana peel, which is a low cost adsorbent. The major advantages of adsorbent over conventional treatment methods are low cost, high efficiency, minimization of sludge etc. Adsorption is recognized as an effective and economic method for low concentration heavy metal waste water treatment. Adsorption experiments were conducted for the removal of heavy metal such as Cr(VI) from synthetic wastewater by using banana peel as adsorbent. Study on adsorption of hexavalent chromium is conducted by varying various parameters like contact time, pH, amount of adsorbent & concentration of adsorbate. The maximum percentage removal of Cr(VI) is obtained in banana peel at pH =2 . Equilibrium time for Cr(VI) adsorption obtained in 40 min .The equilibrium adsorptions data are satisfactorily fitted with various isotherm models such as Langmuir and Freundlich isotherm models. The maximum adsorption capacities are obtained by the application of Langmuir isotherm model as 500 mg g<sup>-1</sup>. Pseudo-second order kinetic model is suitable for describing the adsorption system as compare to pseudo-first order kinetic model. For percentage of Cr(VI) ion removals, gives best results on Batch adsorption study. This study indicates that the Banana peel can be used as an effective and environmentally friendly bio-sorbent for the treatment of Cr(VI) containing waste water.

**Keywords:** Bio-Sorbent, Bio adsorbent, Langmuir Isotherm Model, Carcinogenic Hexavalent Chromium (Cr(Vi)), Banana Peel

### INTRODUCTION

Water pollution raises a great concern nowadays since water constitutes a basic necessity in life and thus, is essential to all living things. The fast-paced development of industries like metal mining operations, fertilizers, and paper industries and pesticides have deliberately discharged various types of pollutants into the environment especially in developing countries. The presence of various pollutants such as industrial effluents, mining and agricultural wastes, sewage, and domestic wastes are continuously discharged into the water system and further affecting our ecosystem due to their lethal effects.

Among other issues, water contamination by heavy metals are more pronounced than other pollutants especially when heavy metals are exposed to the natural ecosystem. Industrialization and globalization have led to the production and disposal of large amounts of heavy metals in the environment. 'Heavy metals' refers to any elements with the atomic weights between 63.5 and 200.6 and a particular gravity



greater than 5.0. The tremendous growth in the utilize of heavy metals over the past decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment. Contamination of soil with heavy metals is one of the great problems of modern societies. A large number of people have been exposed to the health hazards caused by heavy metals present in drinking water, surface water, groundwater, and animal tissue. The toxic effects of heavy metals are made more serious because of their non-biodegradable nature which makes heavy metals pollution a serious environmental problem. Some of these heavy metals are also known to attack the active sites of enzymes in the body, therefore, inhibiting the enzymes. Mining activities, agricultural runoff, domestic and industrial effluents are mainly responsible for the increase of the metals released into the environment.

Effluents from industrial processes such as electroplating, mining, nuclear power operation, battery manufacturing, dye, and pigments have been identified to contain high levels of heavy metals. Such metals include Cr (III), Cr (VI), Zn, Cd, Cu, Ni, Hg, and Pb (Blois et al., 2000). Most of the salts of the heavy metals are soluble in water and form aqueous solution and consequently cannot be separated by ordinary physical means of separation (Alkpokpodion et al., 2010). nearly all heavy metal elements are very toxic when their concentration exceeds their permissible limit in the ecosystem. The high concentration of heavy metals may accumulate in the human body once they interrupt in the human food chain and possibly in effect, cause severe health problems if the metals exceed the permitted concentration.

While hexavalent ( $\text{CrO}_2^{-4}$  and  $\text{Cr}_2\text{O}_7^{-2}$ ) and trivalent ( $\text{Cr}^{+3}$  and  $\text{CrOH}^{+2}$ ) species of chromium are prevalent in industrial waste solutions, the hexavalent form has been considered more hazardous to public health due to its mutagenic and carcinogenic properties. Hexavalent chromium is existing within the effluents generate throughout the electroplating, leather tanning, cement, mining, dyeing, fertilizer, and photography industries and causes severe environmental and public health problems. Hexavalent chromium has been reported to be toxic to animals and humans and it's known to be carcinogenic. Its concentrations in industrial wastewaters range from 0.5 to 270.000 mg /L. The tolerance limit for Cr (VI) for discharge into surface waters is 0.1 mg/L and in potable water is 0.05 mg /L. In order to comply with this limit, its essential that industries treat their effluents to reduce the Cr (VI) to acceptable levels.

A wide range of physical and chemical processes are available for the removal of Cr (VI) from wastewater such as electro-chemical, precipitation, ultra-filtration, ion exchange, electro-dialysis, reverse osmosis, chemical precipitation, and adsorption. The major drawbacks with these processes are high cost, toxic sludge generation, or incomplete metal removal but adsorption has proved to be very effective same commercial activated carbons are utilized as received and also after chemical modifications for Cr (VI) adsorption. More techniques that are cost-effective is still wanting. Also, the idea of utilizing biomass from agricultural and livestock waste as a raw material for the production of activated carbon is the topic of interest for most of the researchers, especially from the agricultural base. Numerous agriculture residues like coconut husk, turmeric waste, Feronia shell waste physic nut seed shell waters, Delonix shell waste, ipomoea Carnia stem, rice husk, jack fruit peel, bamboo, cow dung have been proved suitable for the biosorbent.

The first aim was to find a suitable sorbent for the removal of some Chromium (VI) from wastewater.

Banana peel, a fruit waste were used to produce bio adsorbent through an environment-friendly process. It's causing waste management problems though it has some compost, cosmetics, and adsorbent potentiality. It's an abandoned, readily available, low cost and cheap, environment- friendly bio-material. Considering the above criteria, banana peel was selected to prepare the bio absorbent (Hossain et al 2012).



## 2. OBJECTIVES AND SCOPE OF THE STUDY

The main objective of the work is to evaluate the performance of banana peel as a low-cost adsorbent for the removal of heavy metals from wastewater. With the above-mentioned objectives, the following study plan was made:

- Preparation of adsorbent.
- To find the adsorption edge and optimum pH for the removal of the highest metal.
- To study the batch isotherm parameters and to compare the maximum adsorbent capacity of banana peel with the existing adsorbents.
- To study the thermodynamics of sorption.
- To test the experimental batch kinetics data by using different linearized kinetic rate model.

## 3. METHODOLOGY

Chromium (VI) is one of the most toxic water pollutants and is relatively more toxic than trivalent compounds. Chromium and its compounds are known to cause cancer of the lungs, nasal cavity, and paranasal sinus and is suspected of causing cancer of the stomach and larynx. Hexavalent chromium is transported into cells via the sulfate transport implementations, taking the lead of the similarity of sulfate and chromate with reference to their structure and charge. Trivalent chromium, which is that more common variety of chromium compounds, isn't transported into cells. Cr

(III) is taken into essential mammals for the maintenance of glucose, lipid, and protein metabolism. Chromium can act directly at the location of contact or be absorbed into, or through, human tissue. Chromium (VI) can act as an oxidant directly on the skin surface or these are often absorbed through the skin, especially if the skin surface is damaged. Chromium absorbed into the blood doesn't accumulate in any organs at significant concentrations. In metabolism studies, injected and ingested chromium was found mainly within the liver, kidneys, and blood. Breathing in high levels of Cr (VI) ( $>2 \mu\text{g}/\text{m}^3$ ) containing dust particles in the form of compounds like chromic acid or chromium trioxide can cause irritation to the respiratory system. The permissible limit of Cr (VI) in drinking water is  $50 \mu\text{g}/\text{L}$  and the total Cr is  $100 \mu\text{g}/\text{L}$ .

### 3.1 MATERIALS

This chapter deals with the different materials and equipment used for the study of adsorbents and also describes the various methods adopted for the present investigation.

#### 3.1.1 Glass and plastic wares

All the glassware used in the experiments was manufactured by M/S Borosil Glass Works Ltd. (Mumbai, India) made of borosilicate glass. These are beakers, test tubes, conical flasks, volumetric flask, glass bottles, measuring cylinders, funnels, pipettes, burettes of different capacities. Washing of all the apparatus was done with tap water and distilled water. The cleaned glassware was dried in the air at room temperature.

#### 3.1.2 Instruments

Throughout the project, no. of instruments were used, which were made the analysis quicker and easier. The concentration of chromium solution was determined by using a previously prepared calibration curve at characteristics wavelength  $\lambda_{\text{max}}=540 \text{ nm}$ , using a UV-Visible spectrophotometer which was combined with a computer (HATCH U-2900). Hot air oven used for each time for drying purposes. Sieve analysis was done with the help of different numbers of mesh size sieve.

Instrument Name	Company name/model no
Oven	LG Company MC808WAR
UV-Visible spectroscopy	HATCH U-2900
pH meter	pH system 361 model



Weight machine	ANAMED
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Table 3.1 Name of Instrument

### 3.2 ADSORBENT PROPERTIES

#### 3.2.1 Physicochemical properties of sorbent

Density, Porosity, Specific gravity, bulk density and dry density were determined with the help of specific gravity bottle of 50 ml capacity.

Properties	Banana peel
Particle size	< 5mm
Specific gravity	1.23
Bulk density	8.36
Dry density	5.47
Void ratio	0.775
Porosity	0.436
Surface area	565 .23 cm <sup>2</sup> /g
pH	6.54

Table 3.2 Physical and chemical properties of adsorbent

### 3.3 RAW MATERIAL FOR ADSORBENT PREPARATION

#### 3.3.1 Banana peel

Bananas are a popular fruit consumed worldwide with a yearly production of over 145 million tones in a year. Once the peel is removed, the fruit is often eaten raw or cooked and therefore the peel is usually discarded. Because of this removal of the banana skin, there's a big amount of organic waste being generated. Banana peel, an agro-waste is discarded everywhere the planet as useless material. It is causing waste management problems though it's some compost, cosmetics, and adsorbent potentiality. It is an abandoned, readily available with low cost and environment-friendly bio- material. Banana peels are used as feedstock as they need some nutritional value. Banana peels are popularly used for that purpose on small farms in regions where bananas are grown. The particular nutrition carried in peel depends on the stage of maturity and therefore the cultivar; for instance, plantain peels contain less fiber than dessert banana peels, and lignin content increases with ripening (from 7 to fifteen dry matter). On average, banana peels contain 6-9% dry matter of protein and 20- 30% fiber (measured as NDF). The dry matter, moisture, fat, crude fiber, crude protein, and ash in the dried banana peel were determined to be 90.4%, 9.6%, 5.0%, 11.0%, 10.1%, and 19.0% respectively.

#### 3.3.2 Banana peel

The collected banana peel (Fig. 3.7) were cut into small pieces, size varying less than 5mm. It was washed three times with tap water and with distilled water simultaneously to remove external dirt. The wet banana peel was kept in air for removing the water from the surface and dried in oven at 105°C for 24 hours. The dried banana peels (Fig. 3.8) were grounded into powder and kept in an air tight bottle for further experimental uses.



Fig 3.7 Banana peel before dry



Fig 3.8 Banana peel after dry

### 3.1 ADSORBATE

At first the pseudo industrial waste water is prepared by adding 1.414 g of potassium dichromate solution to 1 liter of fresh distill water to have a chromium enriched water of concentration 500mg/l. This stock solution is then used for further experiments to be done on it.

### 3.2 ADSORPTION STUDIES

#### 3.2.1 Experimental methodology used for the adsorption

Many researchers investigated by following several methods and techniques to stimulate the intimate contact between adsorbent and adsorbate for the maximum up taking of pollutants from aqueous medium. Initially, the calibration curve done before adsorption studies to generate the equation, which implies absorbance is the function of concentration. Broadly, adsorption studies were done in the batch contact system method or continuous flow system method. Here all the studies of optimized operational variables done in the batch contact system method. For all experiments including the adsorption Kinetics, isotherms, thermodynamics, were determined by a batch method which easy and simple to execute.

#### 3.3 BATCH CONTACT SYSTEM ADSORPTION STUDIES

Generally in the batch contact process, a graphically determined amount of adsorbent is agitated with a specific volume of adsorbate solution having known concentration for a certain period of time until the concentration of adsorbate in the solution phase decrease to a desirable level. The removal rate of adsorbate mainly depends upon the force of driving the rate of the adsorption and solution concentration as physical parameters and surface area, the porosity of adsorbent as morphological parameters, acidity or basicity nature of adsorbent also main parameters. Preliminary experimental is done to optimize the adsorbent dose and agitation time.



Fig 3.11 Cr(VI) stock solution



Fig 3.12 Cr(VI) stock solution of different concentration



**Fig 3.13 Weight measurement**



**Fig 3.14 Cr (VI) solution + adsorbent**



**Fig 3.15 Filtration**



**Fig 3.16 diphenylcarbazid**



**Fig 3.17 solution + reagent**



**Fig 3.18 UV-Spectrophotometer**

### 3.1 OPTIMIZATION OF OPERATIONAL VARIABLES

In this section, the effect of various parameters or operational variables such as the effect of adsorbent dose, contact time, pH, initial concentration, and temperature on the adsorption of chromium by different adsorbents have been examined. Kinetics studies for the removal of the Chromium under the given condition have also been studied to understand the mechanistic role of the system. The experiments were repeated twice and the suitable resulting value was reported.

#### 3.1.1 Effect of adsorbent dose

The effect of adsorbent dose on the Chromium adsorption was investigated by varying the amount of adsorbent dose of different adsorbents in a 50 ml chromium solution.

Rice husk adsorbent dose varies between 0.5 to 7 gm and the experiments were carried out at pH 4 using 10 mg/L as initial chromium concentration with contact time exactly 30 minutes. Sawdust adsorbent dose varies between 0.5 to 5 gm and these experiments were carried out at pH 2 using 20 mg/l as initial chromium concentration with contact time 60 minutes. Tea waste powder adsorbent dose varies between 0.5 to 5 gm and experiments were carried out at pH 4 using 10 mg/l as initial chromium concentration with contact time 60 minutes. Banana peel adsorbent dose varies 0.5 to 4 gm and the experiment was carried out at pH 2 using 10 mg/l as initial chromium concentration with contact time 60 minutes. Vegetable peel adsorbent dose varies between 0.5 to 4 gm and the experiment was carried out at pH 2 using 20 mg/l as initial chromium concentration with contact time 30 minutes. The minimum amount of adsorbent corresponding to the cross-section of uptake capacity and percentage removals was attained.

#### 3.1.2 Effect of contact time

The effect of contact time on the adsorption of chromium on different adsorbents was studied in the range of 5 to 60 minutes (5, 15, 30, 60 minutes). The experiment was carried out using banana peel taking dose concentration as 0.5 gm at pH 2 with 10 mg/l chromium concentration of 50 ml.

#### 3.1.3 Effect of pH

Effect of pH on the adsorption of Chromium by different adsorbents was studied in the pH range 2.0 to 10. The pH of chromium solution was adjusted prior to the experiments using 0.1M NaOH and 0.1M HCL. The research was carried out for banana peel, dose concentration 0.5 gm at 10 mg/l chromium concentration of 50 ml with contact time 60 minutes. The pH values of the solution were measured before and after the sorption process and change in pH was observed.

#### 3.1.4 Effect of initial concentration

The effect of initial adsorbate concentration ( $C_0$ ) on the adsorption by adsorbent was examined by varying the initial chromium concentration from 5 to 50 mg/l of 50 ml banana peel. For banana peel, dose concentration 0.5 gm at pH 2 with contact time 60 minutes. The rate-limiting step in the reaction



is defined as the adsorption which is concentration-dependent. When the kinetics of the reaction is controlled by intraparticle transport, Variation in the reaction rate is not expected to be linear, whereas the rates of the strictly adsorptive reaction and simple diffusion-controlled process are expected to be proportional to the first power of the adsorbate concentration.

### 3.1.5 Surface area (particle size)

The adsorbents with smaller particle sizes have a better ability within the adsorption process with an outsized external surface. Therefore more metal ions might be removed than the massive particles. The adsorption increases because the particle size decrease, because the area increases when the particle size decreases. Such an impact is perhaps thanks to the lack of the massive ions to penetrate all the initial pore structure of the adsorbent.

### 3.1.6 Effect of agitation speed:

The adsorbent increases the speed it shows that as the speed of agitation increases, adsorption increases up to a certain speed. After that, it remains constant with respect to change in agitation speed.

## 3.2 MODELING OF ADSORPTION ISOTHERMS AND ITS STUDIES

The process of Adsorption is typically studied through graphs known as adsorption isotherm. It's the graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at a continuing temperature. Within the process of adsorption, adsorbate gets adsorbed on the adsorbent.

To determine the efficiency of the sorbents prepared, the equilibrium sorption of the chromium was studied as a function of concentration. Several equilibrium models have been developed to describe sorption isotherm relationships. The sorption of capacities Banana peel for Chromium has been evaluated by Langmuir isotherm and Freundlich isotherms.

### 3.3.3 Langmuir Isotherm

The most widely used isotherm equation for modeling of the adsorption data is the Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number of identical sites and is given by the following equation.  $q_e = \frac{Q_{max} \cdot b \cdot C_e}{1 + b \cdot C_e}$  (3.8)

where,

$Q_{max}$  = maximum adsorption capacity = monolayer adsorption capacity, (mg.g<sup>-1</sup>), signifies the solid phase concentration, corresponding to the complete coverage of available sorption sites, can be evaluated from the slope of Langmuir isotherm plot (1/q<sub>e</sub> against 1/C<sub>e</sub>) max Q.

b = Energy constant = Langmuir Isotherm constant, (L.g<sup>-1</sup>), this value corresponds to the energy of sorption, calculated from the intercept of the linear plot of Langmuir isotherm.

For solid liquid systems, the Langmuir isotherm is expressed in the linear form as:

$$\frac{C_e}{q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}}$$

$$\text{Or } \frac{1}{q_e} = \frac{1}{Q_{max}} + \frac{1}{bQ_{max}} \times \frac{1}{C_e} \dots \dots \dots (3.9)$$

Generally in Langmuir's theory, the basic assumption is that the sorption takes place at the specific homogeneous sites within the sorbent. The basic assumptions underlying the Langmuir model, which is also called the ideal localized monolayer models, are:

- a) Solute molecules are adsorbed on definite sites on the sorbent's surface,
- b) Each site can accommodate only one molecule,
- c) The area of each site is a fixed quantity determined solely by the geometry of the surface,
- d) The sorption energy is the same at all sites,
- e) The adsorbed molecules cannot migrate across the surface or interact with the neighboring molecules





f) Adsorption may be reversible

The influence of the isotherm shape for ‘favorable’ and ‘unfavorable’ sorption, on the basis of feasibility criteria, was studied by Weber and Chakraborti. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless separation factor, RL, which describe the type of isotherms and is defined by,

$$R_L = \frac{1}{1 + bC_0} \dots \dots \dots (3.10)$$

Where b is Langmuir constant introduced in equation (3.13) and C0 is the initial concentration. The parameters indicate the shape of the isotherm accordingly, if, RL value lies in between 1 to 0, then favorable adsorption indicated. If, RL value greater than 1, unfavorable adsorption, while a value of 1 represents linear & unfavorable and 0 represents irreversible.

### 3.3.4 Freundlich Isotherm

The Freundlich isotherm model is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface, the Freundlich model is non-linear & linear form can be expressed as

$$q_e = K_f(C_e)^{1/n}$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \dots \dots \dots (3.11)$$

Where,

Kf is the Freundlich characteristics constants and 1/n the heterogeneity factor of adsorption, obtained from intercept and slope of ln(qe) vs ln(Ce) linear plot respectively . The value of Kf is an indicator of adsorption capacity and thus can be used for relative measurement of the surface area. b and 1/n are related to enthalpy and intensity of the adsorption. 1/n value should be less than unity for high adsorption capacity.

## 3.4 ADSORPTION THERMODYNAMIC

Thermodynamics applies only to equilibrium adsorption isotherms. Equilibrium means that any point can be reached from either direction by raising (adsorption) or lowering (desorption) the pressure at a constant temperature. Since the adsorption is a kinetic process, the removal rate can be increased or decreased by changing the system temperature. The Gibbs free energy change (ΔG°) of the sorption process is related to the equilibrium constant. And Langmuir constant, b, is also helpful in finding ΔG° for the adsorption process as per the following equation (Rout et.al,2014)

$$\ln \frac{1}{b} = \frac{\Delta G^\circ}{RT} \dots \dots \dots (3.12)$$

Where R is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and T is the absolute temperature.

## 3.5 ADSORPTION KINETICS

The kinetics of sorption is important from the point of view that it controls the process efficiency. The characterization of the sorbent surface is a critical factor that affects the rate parameters and that diffusion resistance plays an important role in the overall transport of the solute. The kinetics of sorption that defines the efficiency of sorption of Chromium were checked by the pseudo-first- order, pseudo-second-order models.

### 3.5.1 Pseudo First Order Model

The first-order rate expression is given by Lagergren

$$\log(q_e - q_t) = \log q_e - K_1 \left( \frac{t}{2.303} \right) \dots \dots \dots (3.13)$$

Where

qt and qe (mg g<sup>-1</sup>) are, respectively, the adsorption capacity at any time t and at equilibrium, k1 is the first-order reaction rate constant (min<sup>-1</sup>) For controlling of kinetics four steps were present,

- (a) Mass transfer of a solute from solution to the boundary film,
- (b) Mass transfer metal ions from boundary film to surface,
- (c) Sorption and ion exchange of ions onto the site,



(d) Internal diffusion of solute.

This step is assumed to be very rapid and non-limiting in this kinetic analysis: sorption is a rapid phenomenon. Using the kinetic equations, the overall rate constant, the forward and backward rate constants were calculated at variable parameter concentration and temperature.

### 3.5.2 Pseudo Second-Order Model

The pseudo 2nd order model can be represented in the following form

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \dots\dots\dots(3.16) \text{ Where } K_2 \text{ is pseudo-second-order rate constant (g/mg .min)}$$

After integrating the equation for boundary conditions  $q_t=0$  at  $t=0$  and  $q_t =q_t$  at  $t=t$ , the following equation is obtained

$$\frac{t}{q_t} = (1/ K_2 \cdot q_e^2) + (1/ q_e) t \dots\dots\dots(3.17)$$

The initial Sorption rate,  $h$  (mg/g.min), at  $t \rightarrow 0$  is defined as:

$$h = K_2 \cdot q_e^2 \quad (3.18)$$

The initial sorption rate  $h$  (mg/g.min), the pseudo second order constant  $K_2$  can be calculated from the slope and intercept of plot  $t/q_t$  vs  $t$ .

$$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t \dots\dots\dots(3.19)$$

Thus the constants can be obtained from the slope and intercept of the linear plot of  $q_t$  versus  $\ln t$ .

## 4. RESULT AND DISCUSSION

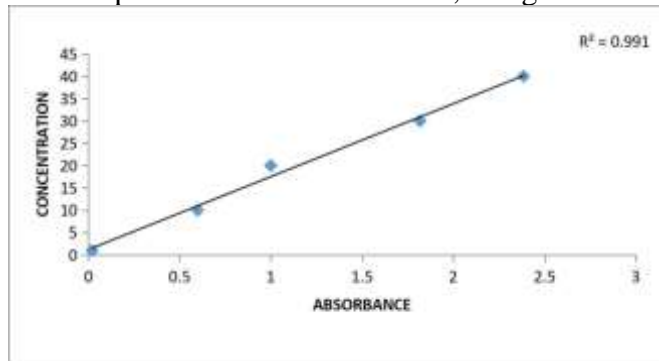
Thorough studies were carried out in order to determine the effects of the operational parameters on metal ion adsorption. The operational parameters studied included the time required for equilibrium, the biomass dose, and the pH of the solution. The uptake of metal ions by the biomass of banana peel was initially evaluated in batch conditions.

### 4.1 CALIBRATION CURVE

A calibration may be a general method of determining the concentration of a substance in an unknown sample by comparing it with the known concentration having a group of the ordinary sample. It knows as analytic signal as due to the calibration curve plotted consistent with the instrumental response and it changes with concentration of the measured substance (analyze). The operator prepares a series of standards across a variety of concentrations near the expected concentration of analyze within the unknown. The concentrations of the standards must lie within the working range of the instrumentation. for many analyses a plot of instrument response vs. analyze concentration will show a linear relationship.

Fig 4.1 Graphical representation of calibrating of unknown Chromium concentration in the water sample,  $C_0 = 1\text{mg/l}$  to  $40\text{ mg/l}$ ,  $t = 27^\circ\text{C}$ ,  $\text{pH} = 2$

The operator can measure the response of the unknown and, using the calibration curve



(Fig. 4.1), can interpolate to find the concentration of analysis or the unknown concentration.

In the calibration curve method, a series of external standard solutions are prepared and measured. A line or curve is fit to the data and the resulting equation is used to convert the readings of the unknown samples into concentration. An advantage of this method is that the random errors in preparing and reading the standard solutions were averaged over several standards. Moreover, non-linearity within the calibration curve are often detected and avoided (by diluting into the linear range) or compensated (by using non-linear curve fitting methods). Most analytical instruments generate an electrical output like a current or a voltage. A calibration curve establishes the connection between the signal generated by a measurement instrument and therefore the concentration of the substance being measured. differing types of chemical compounds and elements give different signals. When an unknown sample is measured, the signal from the unknown is converted into concentration using the calibration curve. Preparation of a series of "standard solutions" of the substance that you simply shall measure, measure the signal, and plot the concentration on the y-axis and therefore the measured signal for every standard on the x-axis. Drawing a line as close as possible to the points on the calibration curve, in order that as many points as possible were right or on the brink of the curve.

#### 4.2 ANALYSIS OF VARIOUS PARAMETRIC EFFECTS ON THE ADSORPTION OF CHROMIUM (VI)

##### 4.2.1 BANANA PEEL

##### 4.2.1.1 Effect of adsorbent dose

The effect of adsorbent doses on the chromium adsorption was investigated by varying banana peel concentration from 0.5g to 5g per 10 ml of synthetic wastewater containing 10mg/l chromium concentration. Other factors are maintained constant. The pH was maintained at 2. Banana peel of 0.5 gm was taken in a flask and synthetic wastewater containing 10mg/l chromium concentration was added and the flask was shaken for 60 minutes. Then it was filtered and stored in a 5ml bottle at room temperature. Its pH was again checked using pH meter and adjusted by adding 0.1N HCL.

The samples were tested for absorbance using a spectrometer. A similar experiment was done by taking banana peel of 1 gm, 2 gm, and 5gm separately and the rest of the parameters remaining the same. The concentrations were found out from the calibration curve and the results were plotted in a graph as shown in Fig. 4.2

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ADSORBENT DOSAGES	1gm	2gm	3gm	4gm	5gm
PERCENTAGE REMOVAL	76.247	78.10	80.63	82.31	82.56
CHROMIUM CONCENTRATION	10mg/lit	20mg/lit	30mg/lit	40mg/lit	50mg/lit
REMOVAL PERCENTAGE(%)	50.14	72.29	84.59	84.60	85.01

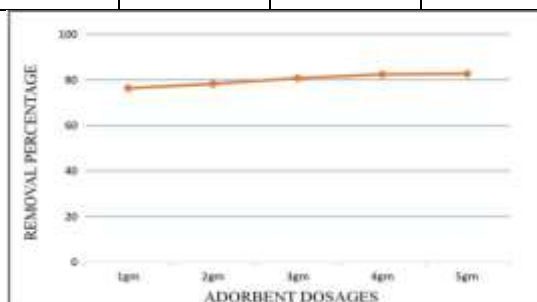


Fig 4.2 Banana peel dosages vs. % removal of chromium by Banana peel

It can be seen that the adsorption rate increases with increase in dose from 0.5g to 5 g due to availability of more surface area and more adsorption functional sites. The percentage removal of chromium concentration found to be 82.56% at 5g dose but the optimum adsorbent dose of 0.5g was chosen for subsequent experiments.

#### 4.2.1.2 Effect of chromium concentration

Initial chromium concentration was varied from 5 to 50 mg/L in order to evaluate the effect of initial chromium concentration on the adsorption capacity of the banana peel. The experiments were performed maintaining all other parameters constant. The experiment was carried out by taking 0.5 g of banana peel in 50 ml aqueous solution of 5 mg/l concentration in 150ml conical flask. The pH was maintained at 2. The flask was shaken manually for 30 minutes. Then it was filtered and stored in a 5ml bottle at room temperature. Similarly, three other samples of 10mg/l, 20mg/l, and 50 mg/l were taken. Its pH was again checked and adjusted by adding 0.1 HCL.

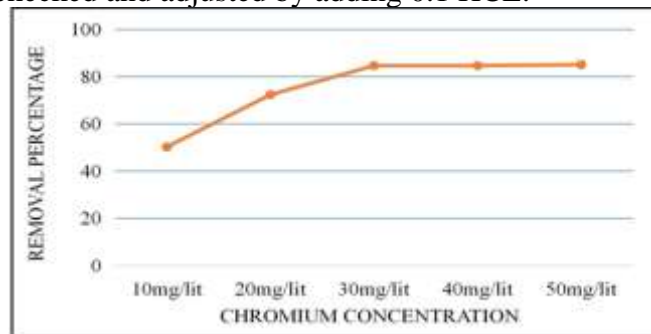


Fig 4.3 chromium concentration vs. % removal of chromium by Banana peel

The samples were tested for absorbance using spectrometer. The concentrations were found out from the calibration curve and the results were plotted in a graph as shown in Fig.4.3.

It can be seen that the peak is obtained at 20mg/l chromium concentration, hence at this concentration; the removal is maximum that is 85.01%. After that there is no significant increase in the percentage of removal of chromium.

#### 4.2.1.3 Effect of time

The effect of contact time on the adsorption of chromium by banana peel was investigated experimentally. The experiment was carried out by taking 0.5g of saw dust in 50 ml aqueous solution of 10 mg/l chromium concentration in 150ml conical flask. The pH was maintained at 4. The flask was shaken manually for 5 minutes. Then it was filtered and the filtrated sample was stored in a 5ml bottle at room temperature. Then the multiple flasks were shaken for 15, 30 and 60 min respectively. Its pH was again checked and adjusted by adding 0.1N HCL.

TIME IN	10 min	20 min	30 min	40 min
% REMOVAL	68.50	71.20	73.29	75.38

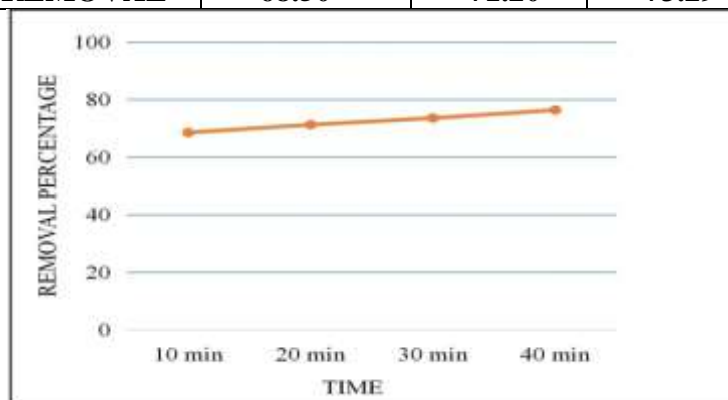


Fig. 4.4 Time vs. % removal of chromium by banana peel

From Fig. 4.4, it can be clearly concluded that the metal removal efficiency increases with the contact time, with the contact time of 60 min can be considered as the optimum contact time to reach equilibrium, resulting in approximately 78.6 % of chromium removal efficiency. At first, the metal removal efficiency increases rapidly and it gradually becomes constant as it approaches the optimum time.

#### 4.2.1.4 Effect of pH

In order to evaluate the effect of pH on chromium removal, the solution of different pH values such as 1, 2, 4, and 6 were taken. Other parameters like shaking time, temperature, concentration, and dose were kept constant. Shaking time of the solution was kept at 60 minutes and concentration was kept 10 mg/l. and the dose was kept 0.5g. Then it was filtered and the filtrate was stored in a 5ml bottle at room temperature. Its pH was again checked using pH meter and adjusted accordingly. The samples were tested for absorbance using a spectrometer.

pH	1	2	3	4
<b>REMOVAL PERCENTAGE</b>	78.58	80.73	74.68	74.32

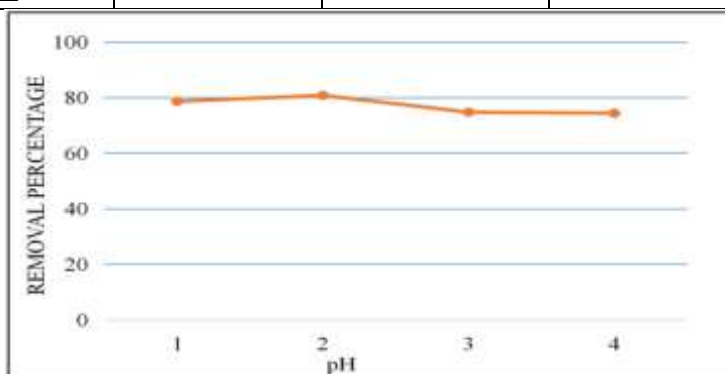


Fig. 4.5 pH vs. % removal of chromium by banana peel

The concentration was found out from the calibration curve and the results were plotted in a graph as shown fig 4.5

From Fig. 4.5, it can be seen that with an increase in pH the percentage of chromium removal decreases. At pH 2, there is a maximum removal of 80.73%.

After that the decrease is gradual. this means that the initial concentration strongly affects adsorption capacity.

#### 4.2.1.5 Effects of agitation speed

To study the effect of agitation speed on the adsorption of Cr(VI) from aqueous solution, agitation speed varied as 90, 110, 120, and 130 rpm. The result shows that as the speed of agitation increases, adsorption increases up to certain speed. After that, it remains constant with respect to change in agitation speed.

Agitation speed(rpm)	90	100	110	120	130
<b>Percentage removal</b>	74.995	78.862	81.334	77.28	76.456

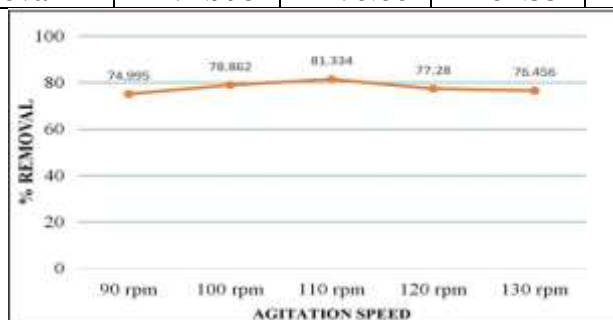


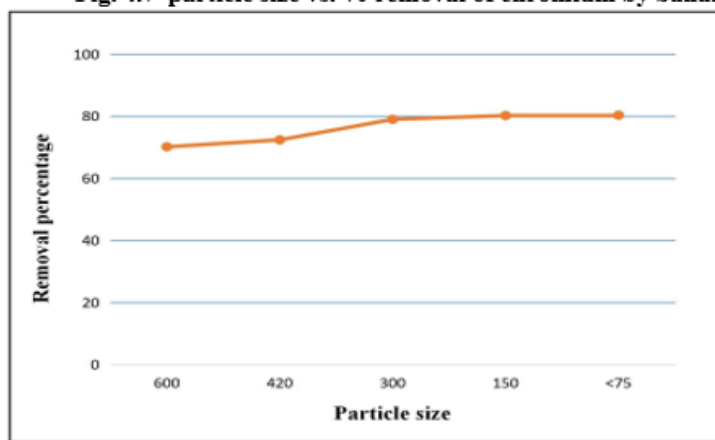
Fig. 4.6 Agitation speed vs. % removal of chromium by banana peel

4.2.1.6 Effect of particles sizes of adsorbent

Batch experiments for the consequences of particles on adsorption were conducted for 6 particle sizes (600µm to <75 µm) at room temperature and pH of 6-6.5 (without adjustment). Fig.4.7 indicates that the removal of copper was increased by decreasing the particle sizes. The percent removal of chromium(VI) increased from 70 to 80% when decreasing particle sizes from 600µm to <75µm. This behavior can be attributed to the effective surface area increased as the particle size decreased and as a consequence, the chromium(VI) adsorption increased. .

Particle size(µm)	600	420	300	150	<75
Percentage removal	70.14	72.39	78.98	80.21	80.32

Fig. 4.7 particle size vs. % removal of chromium by banana peel



4.3 ADSORPTION ISOTHERM STUDY

Equilibrium study on adsorption provides information on the capacity of the adsorbent. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and should even be used to compare the adsorptive capacities of the adsorbent for various pollutants. For this equilibrium study of our work, we've considered basic isotherm models namely Langmuir, Freundlich isotherm models.

The linearized form of Langmuir isotherm is given by equation 3.10 of chapter-3. In figure (4.8) the Langmuir constant  $Q_{max}$  and  $b$  can be calculated by plotting  $1/C_e$  vs.  $1/q_e$ .

The linearized form of Freundlich isotherm is given by equation 3.13 of chapter-3. In figure (4.9) the value of  $K_f$  and  $n$  can be calculated by plotting  $\ln(Q_e)$  versus  $\ln(C_e)$ .

1) Langmuir isotherm

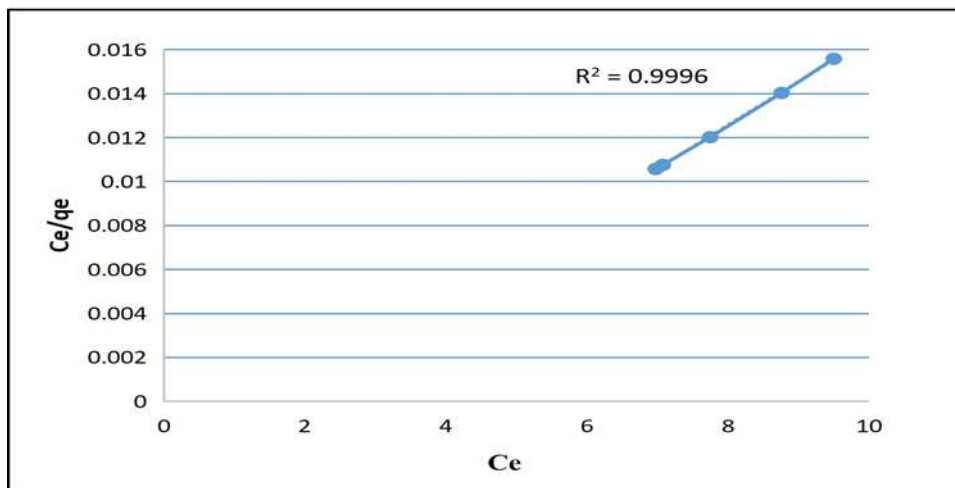


Fig. 4.8 Langmuir isotherm of Banana peel

2) Freundlich isotherm

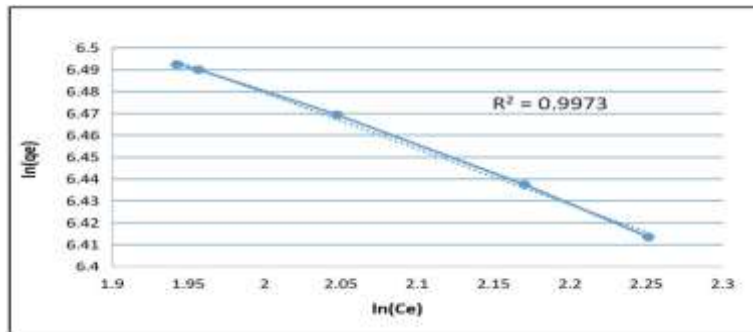


Fig. 4.9 Freundlich isotherm of Banana peel

The correlation coefficient, R2 value for Langmuir model (0.996) is lower than that of the Freundlich model (0.9973), which may indicate the predominance of multilayer adsorption process over intramolecular interactions amongst the adsorbed chromium (VI).

4.4 ADSORPTION THERMODYNAMICS

The impulsiveness of the adsorption process can be analyzed based upon the values of Gibbs free energy changes,  $\Delta G^\circ$ . Langmuir constant, b, is also helpful in finding  $\Delta G^\circ$  for the adsorption process. Where R is the universal gas constant (8.314 Jmol<sup>-1</sup> K<sup>-1</sup>) and T is the absolute temperature 27°C. Based upon Eq(3.14). In banana peel adsorbent the  $\Delta G^\circ$  is -12.865 .

When  $\Delta G^\circ$  is negative, it indicates that adsorption process is spontaneous which necessarily represents the spontaneity of the Cr (VI) adsorption process by banana peel as an adsorbent.

4.5 ADSORPTION KINETICS

The kinetic study of the adsorption process is important as it gives insight into the rate of the adsorption process, which is helpful in finding out the contact time required for adsorption to take place and also facilitates evaluation of reaction coefficients. To investigate the mechanism of adsorption kinetics of Chromium (VI), two kinetic models, namely pseudo-first-order and pseudo-second-order models were analyzed.

The linearized form of pseudo-first-order kinetics is given by equation (3.15) in chapter 3. The values of k1 and we were determined from the graph of pseudo-first-order model that was obtained by plotting log (QE-qt) vs. time shown in figure (4.9). It should give a linear relationship with the slope K1 and intercept of ln(Qe).

The linearized form of pseudo-second-order kinetics is given by equation (3.18) in chapter 3. In figure (4.10) a plot of time Vs. t/Qt should give a linear relationship with the slope QE and with the intercept of K2.

4.5.1 Kinetic of adsorption of Banana peel and Chromium (VI) system

The time-dependent batch adsorption data using fixed-dose 1 gm with pH = 4 maintained of adsorbent at 27°C was used for kinetic modeling of the different Chromium system with an initial concentration of 40 mg-l.

1) Pseudo first order kinetic model of Banana peel

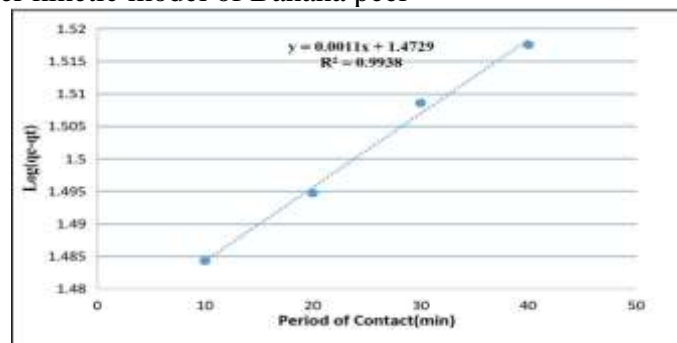


Fig 4.10 Pseudo first order kinetic model of banana peel

2) Pseudo second order kinetic model of Banana peel

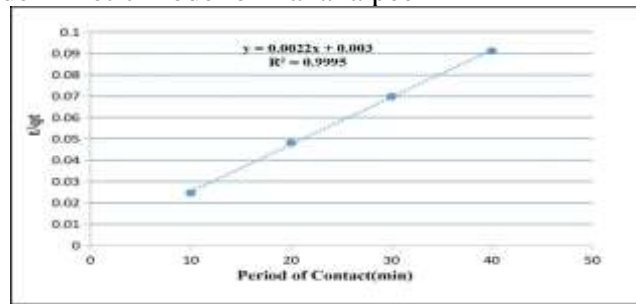


Fig 4.11 Pseudo second order kinetic model of banana peel ADSORPTION KINAMETICS TABLE 4.1

The R2 value for the pseudo-first-order model (0.9938) was lower than that of the pseudo- second-order model (R2=0.9995).Correlation between experimentally observed  $q_e$  value (0.75  $\text{mgg}^{-1}$ ) and that the pseudo- first -order kinetic (12.72 $\text{mgg}^{-1}$ ) was observed with reaction constant

( $k_1=0.002533$ ). Whereas in case of pseudo-second- order kinetic model, the calculated equilibrium adsorption capacity ( $q_e = 0.761 \text{ mgg}^{-1}$ ) was in good agreement with that of the experimentally obtained value ( $q_e = 0.75 \text{ mgg}^{-1}$ ) the reaction constant was found to be ( $k_2=2.18$ ).

5.1 CONCLUSION

Removal of Chromium(VI) from aqueous solutions by adsorption using banana peel and has experimentally determined. The prepared adsorbent was characterized by different analyses and tests. From our studies, it was found that banana peel adsorbents are a promising material for effective removal of chromium. By adopting this methodology the following benefits can be achieved:

1. As this treatment process uses low-cost food, industrial and agricultural wastes as adsorbents we can use them for the large scale treatment of waste as well as domestic water.

Adsorbent	$q_e(\text{Exp})$	$q_e(\text{C}1)$	$k_1$	R2	$q_e(\text{C}1)$	h	$k_2$	R2
Banana Peel	0.75	12.72	0.00253	0.9938	0.761	7.349	2.18	0.9995

2. Toxic effects of industrial wastes can be reduced to a significant extent thereby reducing the negative impacts on aquatic life.

3. Solid waste management can be diligently performed using these solid wastes as adsorbents.

4. The amount of land needed for the effective disposal of solid wastes can be reduced.

The following conclusions are derived from the experimental investigation .

- For Cr(VI) and banana peel system

Based open the experiment it can be calculated that by varying the pH, adsorbent dose, agitation speed, particle size, chromium concentration, time; the maximum % of removal of Cr (VI) was obtained at pH 2 80.73 %, at 50mg/l chromium concentration

85.01 %, at <75 particle size 80.32%, at 110 rpm agitation speed 81.34%, at 5gm banana peel does 82.56 % and at 40 minutes 75.38% respectively. As pH =2 set as an optimum value, adsorption for this system took place in a highly acidic environment.

Uptake capacity increase with the increase of initial chromium concentration and time concentration.

5.2 FUTURE SCOPE OF WORK

- The following recommendation is made for further studies
- Adsorption studies of Chromium (VI) using other self-prepared or commercial adsorbents.
- More detailed characterization of self-prepared adsorbents must be performed.
- Optimization of process/operation variables using the statistical procedure.





- Adsorption studies will investigate through the continual flow system method and fluidized bed system even be performed for the best utilization of this adsorption process.

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