

The use of GAC as an Adsorbent for the Removal of Heavy Metal Ions from Aqueous solution using Batch Adsorption study.

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ABSTRACT

One of the biggest issues facing the globe today is environmental contamination, especially from heavy metal ions in wastewater. When seeking corrective action, a number of traditional techniques like heavy metal ions have so far been eliminated by ion exchange, chemical precipitation, coagulation, membrane separation, reverse osmosis, and adsorption techniques. To remove various heavy metal ions from wastewater, especially those that have been harmful to living things, a wide range of adsorbents have been created. In comparison to conventional methods, adsorption procedures are inexpensive and offer a high removal effectiveness of heavy metal ions, even at trace levels. For the adsorption of heavy metal ions from wastewater, it has been essential to produce inexpensive and easily accessible adsorbents. The adsorbents can be gathered from industrial byproducts, animal dung, and agricultural waste. By their very nature, all adsorbents feature functional groups that are essential to the adsorption of metal ions. Chemically modified adsorbents often have a larger surface area and a better adsorption capacity than unmodified adsorbents. A number of natural waste materials and their modified forms have been assessed in this evaluation for their ability to remove different metals from wastewater and drinkable water. The gathering of thorough knowledge regarding the application of inexpensive adsorbents for the removal of heavy metal ions has been the main focus.

Keywords: Granular Activated Carbon (GAC), Heavy Metal Removal, Adsorption, Wastewater Treatment, Nitric Acid Modification

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Introduction

The discharge of toxic heavy metals into the environment poses a significant threat to the quality of water and aquatic ecosystems, endangering human health [1-2]. Trace elements such as arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn) are recognized as metallic pollutants in wastewater, industrial effluent, and sewage sludge [3-6].

A number of pollutants – both organic and inorganic – causes harm to the environment. The present world faces the risk of heavy metal ions most since they are very toxic and carcinogenic in nature. The pollution from heavy metals is a result of human activities and the consequence on the food chain of the ecosystem. Heavy metals are released into environment from various sources such as chemical industries, textiles, tanneries, plastics, mining, battery manufacturing, paints and pigments, paper and pulp industries, etc., [7-10]. Release of toxic metals into water stream is a serious concern, which may affect the quality of water supply [11]. Some of the hazardous heavy metal ions which pose potential danger threat to human health are arsenic, mercury, chromium, cadmium, and lead. Heavy metal ions noted are not recyclable and accumulate in living organisms [6]. Several past disasters for the contamination of heavy metals in waterbodies include: 'Itai-Itai' for pollution of cadmium in Jintsu river of Japan

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and 'Minamata tragedy' due to methyl mercury contamination in Japan [12]. These have been an ever increase in the use of heavy metal ions due to rise in industrial activities to cause increased pollution of water streams day by day. Because the heavy metal ions are not biodegradable, they are potent toxins. Moreover, heavy metal ions are carcinogenic in nature. Alarming, the heavy metal ions in water systems are at higher concentrations than the permissible limits to cause numerous diseases concentrations above the allowable limits could result in a variety of illnesses [13]. A lot of techniques, e.g. filtration, ion exchange, chemical precipitation, reverse osmosis, etc., have been developed in the waste water treatment, but in some cases they cannot provide successful removal of the ions or their application is very expensive. Thus, adsorption, as a simple, adaptable, and low cost method is considered to be a convenient route in the control of the water effluence [14], especially handling low concentration waste streams and meeting severe treatment levels [15]. Wide range of adsorbents, such as zeolites, clay, biomaterials, industrial or agricultural wastes, etc., considered as inexpensive adsorbents, and accessible in big amounts, have been suggested to be very effective for the toxic metals removal in the waste water treatments [16]. On the other hand, the purification of water using carbons has been used for ages. Further more, the high surface to volume ratio makes activated carbons very attractive for effluent water pollutants removal [17].

Materials and Methods

- 1) **Power requirement** : All power needed for running electric appliances was obtained from an Automatic Servo stabilizer, 5 KVA capacity (M/s Dandekar Electricals Pvt. Ltd., Nagpur).
- 2) **Distilled water** : The present work involved estimation of metal ions in solution and hence good quality of distilled water was necessary for preparing experimental solutions. The distilled water obtained from laboratory distills water still (M/s. Kumar, Industries Mumbai, Capacity 1.5 lit/hour). Distilled water thus obtained was preferably prepared a fresh before use, as and when needed, and stored in a Borosil 5 liter flat bottom flask provided with a glass stopper.
- 3) **Glasswares** : All glasswares in laboratory were standard glass wares obtained from M/s Borosil, Bombay. Before use these glasswares were thoroughly washed with chromic acid & several times with distilled water & dried in oven.
- 4) **Electric Oven** : In this laboratory NEOLAB electric oven was used which had an arrangement to regulate the temperature to the required value.
- 5) **Balance** : The balance used for weighing was a electronic balance with an accuracy of +
- 6) **Mechanical Shaker** : A mechanical shaker (Remi Model No. RS-24, Remi Instrument Ltd., Mumbai) was used for agitation of GAC with solution for some adsorption experiments. The shaker was especially useful for adsorbing the metals on Granular Activated Raw Carbon and Granular Activated Oxidized Carbon. Usually the experimental samples could be shaken for around 12 hours, but for certain system it was necessary to shake it for longer periods. For this purpose an electronic timer was fabricated in this laboratory with the help of electrical engineering section of this Institute. This timer helped in switching on the shaker for approximately 3 minutes while switching it off for same period during the next 3 minutes.
- 7) **pH Meter** : The digital pH meter used in this laboratory was an LI-120 model (M/s ELICO, Pvt. Ltd. Hyderabad, India) and standardized using potassium hydrogen phthalate buffer of pH 4.01 at 25° C.
- 8) **Spectrophotometer**: All Spectrophotometer measurements were done on a Systronics Digital Spectrophotometer Model 166, India Ltd that was readily available in this laboratory using 1 cm matched cuvettes.
- 9) **Thermostat Bath** : A thermostat arrangement, which was an essential requirement for agitating the loaded carbon with metal ion solution and for all subsequent kinetic runs was fabricated in the laboratory using a 50 liter plastic through which employed distilled water and had provision for heating and cooling of the bath liquid. With the help of a contact thermometer the heater & the cooling pump were operated through an electronic relay separately. By this help, all systems run at a uniform temperature of $28^{\circ} \pm 0.1^{\circ}\text{C}$. Since the temperature in the course of experimentation was usually above the ambient temperature of the laboratory for most parts of year, it had to be cooled, for this purpose an old refrigerating unit provided with a heavy-duty compressor was employed. The cooling coils of the unit were dipped in a bucket of water. Cold water produced by this unit was circulated with the

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help of circulating pump through the thermostat bath liquid and with such a unit it was possible to run the thermostat continuously at the temperature of $28^{\circ} \pm 0.1^{\circ}\text{C}$ during the entire work. Once all these facilities were readily available it was possible to plan adsorption studies as also to carry out rate of adsorption in the present work.

10) Determination of adsorption isotherm of Nickel on different grades of granular activated carbon.

For determining the adsorption isotherm of nickel ion on different grades of granular activated carbon like F-400, F-300, F-200, F-100 varying weight of GAC was taken into a 1 liter round bottom flask carefully for each set of experiment, and fixed concentration of 200ml of nickel ion in solution was then introduced. The stirrer was placed in position and the contents were stirred for six hours at 28°C . The initial and final concentration of nickel ion in mg/lit was then determined spectrophotometrically. Usually equilibrium was reached with the period of shaking for six hours. Using both values C_0 and C_e , the value of q_e , the amount of nickel adsorbed on the GAC was determined by following expression.

The selection of suitable activated carbon is an integral part of the design of a carbon treatment plant. Although there are a fair number of manufactures of fibrous activated carbon, granular activated carbon, and also the powdered activated carbon, many of these carbons are not necessarily suited for wastewater treatment system. In addition, some granular activated carbons have an advantage over the other in adsorption capacity depending on the adsorbate to be adsorbed, physical durability, operating characteristics and costs.

This chapter highlighting methods employed and experimental techniques in studying the adsorption of metals as Ni^{2+} , Cu^{2+} , Co^{2+} , $\text{Cr}_2\text{O}_7^{2-}$ on several grades of Granular Activated Raw Carbon.(G.A.C.) and Granular Activated Oxidized Carbon carried out by batch experiment and fixed bed column studies..

The present work required some prerequisites in the laboratory to enable smooth experimentation.

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(I) Choice of adsorbent from the various grades carbons available in this laboratory.

Activated carbon plays very important role in all wastewater treatment technology. Various grades of carbons readily available in the laboratory were the Calgon Corporation Filtrasorb varieties namely F-400, LCK, RRL, Lurgi (German) because of the availability in large quantity of Filtrasorb varieties (M/s Calgon Corporation, Pittsburgh, U.S.A.) were utilized in the laboratory work, than other varieties like Lugi, RRL, and LCK.

The various grades of Calgon Corporation Filtrasorb as mentioned above were used adsorption studies. The advantages of this selected adsorbent was as follow

- a) Easy availability of the carbon and mesh size of the carbon.
- b) They had varied pore structure, pore volume and surface area and they are prepared from the same starting material, namely bituminous coal.
- c) Sufficient quantity of carbon to last for the entire work.
- d) Resistance of the carbon to abrasion in the work.

(III) Preparation of the Solution of metal ions and their estimations.

A) Preparation of solution of Nickel ion and its estimation

A standard stock solution was prepared by taking 1.401 gm of Nickel Sulphate (E. Merck India Ltd.) and dissolving it in 500ml of distilled water. 10ml each of this stock nickel solution was taken in different conical flasks. To it a pinch of solid indicator (Eriochrome Black T+Potassium Nitrate) was added followed by 4ml of 1M NH_4Cl solution. Concentrated ammonia solution was then added drop wise to make the solution strongly alkaline and the color of the solution turned yellow. It was then titrated against a standard 0.01M EDTA solution when the color changed from yellow to violet at the end point. The amount of nickel in solution was calculated using standard procedure [21]. Working standard solutions were prepared by appropriate dilution of stock solution as incase of copper solutions. For Beer's Law plot dilute nickel solution of the concentration range of 10^{-4} M was taken in 10 ml aliquots in different small conical flasks. To it 2 ml of Bromine water was added followed by 1 ml of the 50 % ammonia solution. It was then kept for sometime and 1 ml of 1 % DMG solution in absolute ethanol was added when a red coloration was developed. The absorbance of above solution was measured at 445 nm against a reagent blank [2]. The reagent blank contained all other solutions added above except the nickel solution. The total volume of the solution was maintained constant to 10 ml by adding distilled water. A graph plotted between absorbance versus concentration of the nickel in solution represents a standard Beer's Law. A working equation was derived from the above Beer's law for use in all calculations. The Beer's Law data and working equation are given in **Table**

(IV) Modification of carbon surface with oxidizing agent

In the present work carbon surface was modified by two ways The granular activated carbon adsorbed with metal ion was first incinerated in a muffle furnace at $800^{\circ}\text{C} \pm 15^{\circ}\text{C}$, when it was completely converted to the oxide. The oxide was then leached with 10ml of concentrated nitric acid and diluted to a constant volume. An aliquot of this solution was used for colorimetric analysis of the corresponding metal. The above process however proved unsatisfactory in a majority of cases. Hence oxidizing the surface carried out the second process of modification. In this process the nitric acid was used as an oxidizing agent.

Granular activated carbon modified by concentrated nitric acid and this process is called as chemical modification of the carbon surface, which involved following procedure. In this case about 10 gm of carbon was taken in conical flask and add 30 ml of concentrated nitric acid. The flask was covered with glass stopper and was kept overnight. It was then boiled 50 minutes by adding a little distilled water. After cooling the contents of the flask was decanted

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carefully and the residual carbon was washed several times to rid it of all adhering acid. This modified carbon was then agitated with metal ion solution having single system. It was found that there was an increase the adsorption capacity of carbon.

Recovery of adsorbed metal ions from the Granular Activated Carbon surface.

As discussed above the transition metals are scavenged by granular activated carbon, it was thought if simultaneous recovery of these metals could be possible. For the recovery there was a need to modify the carbon. The carbon was modified in two ways as discussed earlier. In second modified process the GAC containing metal ions after stirring was filtered off and was air-dried. The carbon was then transferred into small conical flasks and 10ml concentrated nitric acid was added to each flask. It was then boiled for 15-20 minutes by adding a little distilled water for sometime. The carbon was then filtered off, and washed; the filtrate and washings were diluted to a constant volume. An aliquot of this solution was analyzed calorimetrically for the determination of metal ions. The results are given in **Table**

(VII) Experimental arrangement and method for carrying out adsorption studies

To determine the adsorption isotherm of co-metal ions Nickel a water thermostat bath was used. All adsorption equilibrium experiments were carried out in 50-liter tub bath, in batches of six units at a time. Each arrangement consisted of one liter round bottom corning flasks held in the bath with a clamp and had arrangements for stirring the contents of the flasks. The contents were stirred using a paddle type glass stirrer with the help of Remi stirrers (Model RQ 122) whose speed could be regulate by any desired value. The temp of the bath was maintained by heating or by cooling and controlled to 25°C with the help of thermometer through an electronic relay. The temp regulating accuracy was within $\pm 0.5^\circ\text{C}$.

At first, a one liter of round bottom flask was introduced into the tub bath and different weights of GAC or OGAC (Oxidized Granular Activated Carbon) 0.1 gm to 1 gm carbon each time was stirred with 200 ml each of same concentrations of metal ions in this flask using the glass paddle stirrer fitted to the Remi motor. The ratio of length of paddle/diameter should lie between 0.2 to 0.55 suggested by Wand Gray J. B. and also suggested that the width of the blade to its length should be between 0.25 to 0.16 and the sped of the stirrer should be 1000 rpm and the length of the glass stirrer was fixed at 25 cm. Paddle size used was 3.2 cm x 1 cm x 0.3 cm and constructed from a Teflon piece.

The solution was stirred for about 5 to 6 hours to achieve equilibrium at the constant temp (28°C). The initial and final concentration of metal ion was determined spectrophotometrically as indicated earlier and the amount of metal ion adsorbed by the particular GAC calculated using std expression.

W = Weight of carbon taken in grams.

(IX) Determination of adsorption isotherm of Nickel on Granular Activated Carbon.

For determining the adsorption isotherm of nickel ion on different grades of grades of granular activated carbon like F-100 varying weight of GAC was taken into a 1 liter round bottom flask carefully for each set of experiment, and fixed concentration of 200ml of nickel ion in solution was then introduced. The stirrer was placed in position and the contents were stirred for six hours at 28°C. The initial and final concentration of nickel ion in mg/lit was then determined spectrophotometrically. Usually equilibrium was reached with the period of shaking for six hours. Using both values C_o and C_e , the value of q_e , the amount of nickel adsorbed on the GAC was determined by following expression.

$$q_e = (C_o - C_e) \times V/W$$

Where

q_e = Concentration of metal ion on GAC in mg/gm of carbon

C_o = Initial concentration of metal ions in solution in mg/liter.

C_e = Equilibrium concentration of metal ions in solution in mg per liter.

V = Volume of solution taken in liters.

Thus for each GAC- Chromium ion system there is available a set of data for q_e and C_e . A plot q_e versus C_e then represents a typical adsorption isotherm for the nickel ion on different grades of GAC. The data on these isotherm are given in **Table** , as also $\log q_e$, $\log C_e$ and $1/q_e$ and $1/C_e$ values for which are useful test for adherence

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of adsorption of chromium ions to either the Freundlich or the Langmuir adsorption models. The isotherms and the adherence to Freundlich and Langmuir theories are given in Fig.

ADSORPTION ISOTHERM OF METAL ION ON MODIFIED GAC.

Modification of Granular Activated Carbon with Concentrated Nitric Acid

In the present work an effort has been made to modify the carbon surface by using oxidizing agents called as chemical modification of the surface. To modify the carbon surface concentrated nitric acid is used. When raw F-100, F-200, or F-300 of carbon was treated with concentrated HNO₃ as described in previous chapter and allowed to agitate with metal ion solution for both single and multi solute adsorption system, it was observed that the adsorption capacity of the carbon had increased.

The adsorption isotherms of metal ions like Cr, Ni, Co and Cu on various grades of oxidized GAC i.e F-100. These results are summarized in Tables and Fig. These Figures at equilibrium show a plot of solid phase concentration of metal ions (mg/gm) versus the equilibrium concentration of metal ions in solution (mg/lit). The equilibrium was attained in 6 hours as observed by test experiments. This was verified by conducting the experiments for prolonged periods of time, until no detectable changes in equilibrium concentration values C_e could be observed. An equilibrium between the adsorbate in solution and the adsorbate on the carbon, there is a definite distribution of the adsorbate between the solution and the solid phase which is also a measure of the position of the equilibrium in the adsorption process. A relation who governs these two aspects is referred to, as an Adsorption Isotherm. The relation between these two quantities under isothermal condition is called as an adsorption isotherm. i.e. plot of q_e versus C_e. q_e is calculated by using the expression.

Experimental arrangement for studying kinetics of adsorption of metal ions on granular activated carbon.

The procedure for kinetic study of nickel ion uptake by grades of GAC was carried out utilizing 1 liter Borosil flask containing 1 gm of granular activated carbon. 500 ml of the nickel ion solution was taken whose concentration was equivalent to the concentration that was on the descending portion of the lot of q_e versus C_e on the adsorption isotherm curve i.e. where curve just starts showing constancy in the value of q_e. This solution was taken into the round bottom flask without distributing the accumulated carbon granules. The glass stirrer was set in motion at a RPM of 1000 when carbon granules were drawn into the solution and the time noted. After every 15 minutes 5 ml samples of the solution were withdrawn for the first hour and after every 30 minutes interval for the remaining three hours. The entire experiment lasted for 4 hours. The concentration of the nickel ion the solution withdrawn at these definite time intervals were estimated spectrophotometrically which were designated as C_t.

The values of the concentration of the nickel ion on the loaded granular activated carbon at the same time intervals was estimated using a similar expression as before [22-24]

$$q_t = (C_o - C_t) \times V/W$$

Where

q_t = The concentration of nickel ion on the GAC in the mg/g at a particular time interval C_o = The concentration of the solution at start in mg/lit

C_t = The concentration of the nickel ion in the solution at any time t in mg/lit.

W = Weight of carbon taken in gm

V = Volume of nickel solution in liters.

Result and Discussion:

The rate of adsorption of the nickel metal on different grades of carbon and data represents in Table.

Values of the q_t at different time intervals were then plotted versus these time intervals. q_t^{*} represents the equilibrium concentration of metal ion on the loaded GAC at a particular time interval, calculated using determined values of C_t and using the plot of q_e versus C_e finding q_t^{*} at C_e=C_t which was q_t^{*}. A plot both q and q_t^{*} were plotted versus different time interval. These curves represents the approach to equilibrium as shown in figure. The difference between the values of q_t^{*} and q_t at any time represented the driving force operative in the process leading to adsorption on the Granular Activated Carbon. The data for C_t, q_t^{*} and q_t are given in Table for

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the four grades of Raw Granular Activated Carbon and oxidized Granular Activated Carbon. These Tables also give calculated values of dq/dt calculated at the various time intervals using a computer program developed in this laboratory. At the same time intervals selected values of $(q^{*2} - q)/2q^*$ and $(q^* - q)$ were also computed from q^* and q values which were useful to test adherence to the Linear Driving Force (LDF) and Quadratic Driving Force (QDF) Models.

Table 1

Sr. No.	Metal ion	Type of Carbon	Grades of GAC	Q ^o g/mg	A 10 ⁻¹⁶ cm ²	S cm ² /gm	S' cm ² /gm
1	Ni ²⁺	Raw	F-100	45.4545	5.244	1.436 x 10 ¹⁰	1.51 x 10 ¹⁰
2	Ni ²⁺	Modified	F-100	111.111	5.244	3.509 x 10 ¹⁰	3.296 x 10 ¹⁰
2							

Discussion of Kinetics of Exchange of Chromium with GAC

The data for uptake of metal ions adsorbed on raw GAC or oxidized GAC are given in **Tables**

Film diffusion is importance in solution containing high adsorbate to solvent ratios and can be rate controlling in such processes. If adequate provisions are not made to include this aspect in the basic diffusion equation, it might lead to gross errors in evaluation of the diffusion coefficient and a misrepresentation of the actual process. Literature has indicated the importance of film diffusion in detail [6]. All experiments in the present work were carried out at a RPM of 1000. This RPM is much higher than the speed of stirring which could affect the concentration versus time plots. In the present investigation the effect of film diffusion could be neglected at $t > 0$ since it since it was verified in this work that when the dimensionless concentration parameter C/C_0 is plotted versus time, a measure of film diffusion co-efficient could be evaluated from the slope of curve at $t = 0$. On comparing this with the value of the calculated particle phase mass transfer coefficient using QDF approximation as mentioned at a later stage, it was observed that former values are much higher thereby indicating that film diffusion parameters are to be neglected in the present case. Further the profile of 'C' versus 't' plots did not vary with the speed of the stirrer greater than RPM 800 showing elimination of film diffusion in the present cases [7]. For kinetic studies of the Nickel ion uptake by grades of GAC, 1 gm of GAC was taken in a 1 liter of round bottom flask. 500ml of the nickel ion solution at a desired concentration was then introduced to it carefully and stirred with the help of a glass stirrer. The time of addition of carbon was noted as time $t = 0$. Thereafter aliquots of 5 ml of chromium ion solution each time were withdrawn at regular intervals by momentarily interrupting the stirrer. The first four readings were taken at 15 minutes time interval; next two readings were taken at a time interval of one hour. The initial concentration of nickel C_0 and the concentration of the nickel at different time intervals C_t was estimated by the procedure outlined in the experimental chapter using the standard Beer's law plot and with the working equation established.

GAC is generally considered to be diffusional in character in all cases of adsorption. Since stirring the carbon particles and metal ion solution at a RPM of 1000 has eliminated the film diffusion resistance, the problem restricts itself to particle phase diffusion. One or more of several diffusion steps determines the effective rate of adsorption by carbon. Individual steps in the transport mechanism, which may restrict the overall performance in a certain region operating condition, follow the sequence.

- i) Mass transfer from the bulk liquid to external surface of the adsorbent.
- ii) Pore diffusion in the fluid phase occurring within the adsorbent.
- iii) Reaction leading to adsorption on the surface of the adsorbent, and
- iv) Diffusion in the sorbed state on the surface of the adsorbent (surface diffusion).

It has generally been recognized through experimental evidence that the above-mentioned sequence occurs in series. Sometimes both pore diffusion and surface diffusion occur simultaneously and the faster one amongst the two controls the rate.

In order to analyze a typical rate data i.e. concentration of adsorbate versus time plot, it would be necessary to either rigorously include all the above four steps or exclude some of them by suitable experimental conditions

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within the contacting equipment, will not be the rate determining process. This may be excluded in any rigorous mathematical treatment.

The elimination of the effects due to step (i) has attracted attention of several workers. However this aspect is of importance to chemical engineers. In general step (iv) is more likely to control systems with high solute concentrations and (i) and (ii) are likely to influence the rate for low total fluid phase concentration. The possibility occurring within the contacting equipment, which might affect the rate, can be taken care of by using the same apparatus and working condition for all experimental work under test.

Diffusion, results from a concentration gradient either in the fluid phase or on the solid phase. Where diffusion involves separation of the solute from the fluid phase to sorbent phase it is called particle phase diffusion or homogeneous diffusion described by an effective diffusion coefficient D . The driving force for pore diffusion which usually occurs within the pores of the adsorbent is due to the concentration gradient of the adsorbate in the pore space, and is characterized by a pore diffusion coefficient D_p . Alternatively surface diffusion which occurs after adsorption due to the migration of adsorbed molecules along the pore wall may be represented in terms of the gradient of amount of adsorbate on the pore wall. This is characterized by a surface diffusion coefficient D_s .

It is frequently encountered that one of the two types of the above mentioned diffusional processes could be treated under certain specified conditions, which are specific to the cases. Several workers have estimated pore diffusivities in an agitated tank, while some have proposed a method where surface diffusion is rate controlling [8] This method has subsequently undergoes change [9] A detailed review of the various methods available in literature [10] does not tell which of the above two diffusional process is predominant in a particular system. However, by reasoning only, it could be predicted which of the two the pore and the surface diffusion could be rate controlling, within the limits of experimental accuracy.

Unsteady state diffusion in spherical particles plays an important role in design of adsorption columns. The appropriate partial differential equation is

$$\frac{dq}{dt} = \frac{1}{r^2} \frac{d}{dr} \left[D r^2 \frac{dq}{dr} \right]$$

Where q = represents solid phase concentration of the adsorbate

D = Diffusion coefficient in solid phase

r = radial distance.

Analytical solutions of this equation are available elsewhere in literature [18]

The solutions assumed a number of simple boundary conditions and constant D but are not easy to use. For this reason Glueckauf and Coates [12]. first suggested the Linear driving force (LDF) approximation. In this method the rate of adsorption by a spherical particle is considered to be the product of surface area, an effective mass transfer coefficient and a driving force consisting of the difference between the bulk average concentration in the spherical particle q and the surface concentration q^* . Hence this equation can be written:

$$\text{Rate} = \frac{4}{3} \pi a^3 \frac{dq}{dt} = 4 \pi a^2 K_p (q^* - q)$$

Where a = radius of the spherical particles.

This differential equation is much easier to deal than the differential equation mentioned above and also gives analytical solutions.

Glueckauf later presented justification of this equation and also gave an indication of the conditions under which it is valid. If q_0 represents initial concentration of the adsorbed species on the spherical particles plunged at $t = 0$ into a well stirred fluid of constant composition and if final steady state concentration in the solid (in equilibrium with the fluid) is q_∞ , then he showed that

$$q - q_0 = \dots\dots\dots(4)$$

He was then able to make certain approximations and showed that

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$$dq/dt = 15D (q^* - q)/a^2 \text{-----(5)}$$

This is most commonly quoted from of the LDF equation. It can be easily seen from the above relation that

$$K_p = 5D/a$$

This LDF equation (5) can be applied for cases where the adsorption isotherm was linear or moderately curved and adsorption took place under conditions close to equilibrium. Review of various references mentioned in literature clearly indicated that the LDF method although simple, leads to an estimate of gross diffusion. Further it is an useful method to know the adsorption processes and helps considerably in designing adsorption systems. Further it is a useful method to know the adsorption processes and helps considerably in designing adsorption systems. It might be worthwhile assessing the equation for initial time periods when $t = 0$. In such situations the equation (5) suggests that dq/dt approaches a large infinite value while the right had side remains numerically finite [19]. To overcome the anomaly mentioned above namely the large rise in dq/dt when it approaches zero, Vermeulen [20]. proposed the following QDF expression.

$$Dq \text{-----(6)}$$

System G.A.C .F-100 Raw Carbon-Ni²⁺
Temp = 28° ± 0.1° C
Volume of solution =500ml

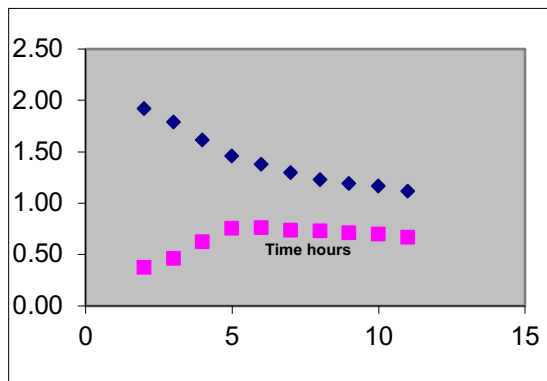
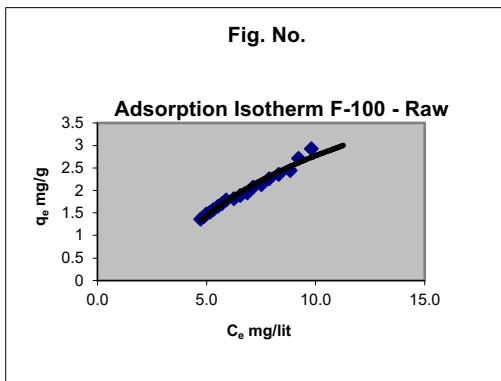
Sr. No.	Time hours	Conc. mg/lit	q mg/g	q*mg/g	(q*-q)	dq/dt	(q* ² -q ²)/2q
1	0.00	7.749		2.20			
2	0.25	6.883	0.433	2.00	1.57	0.3759	4.4032
3	0.50	6.716	0.516	1.90	1.38	0.3509	3.2366
4	0.75	6.564	0.592	1.85	1.26	0.3259	2.5929
5	1.00	6.409	0.670	1.82	1.15	0.3009	2.1378
6	1.50	6.135	0.807	1.78	0.97	0.2509	1.5592
7	2.00	5.918	0.916	1.75	0.83	0.2009	1.2143
8	2.50	5.722	1.013	1.70	0.69	0.1509	0.9193
9	3.00	5.713	1.018	1.69	0.67	0.1231	0.8939
10	3.50	5.704	1.023	1.65	0.63	0.1131	0.8200
11	4.00	5.505	1.122	1.64	0.52	0.0010	0.6372

Kinetics of Removal of Ni²⁺ From Solution
System : G.A.C. Oxidised Carbon - F-100
Temperature = 28° ± 1° C
Volume of Solution= 500 ml

Sr. No.	Time hours	Conc. mg/lit	q mg/g	q*mg/g	(q*-q)	dq/dt	(q* ² -q ²)/2q
1	0.00	6.003		5.20			
2	0.25	5.595	0.204	4.90	4.70	0.4938	58.6901
3	0.50	5.240	0.381	4.70	4.32	0.4500	28.7659
4	0.75	4.950	0.526	4.40	3.87	0.3054	18.1248
5	1.00	4.867	0.568	4.20	3.63	0.2541	15.2402

The use of GAC as an Adsorbent for the Removal of Heavy Metal Ions Ion from Aqueous solution using Batch Adsorption study.

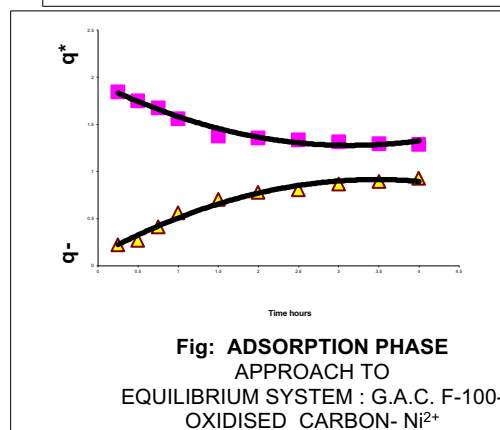
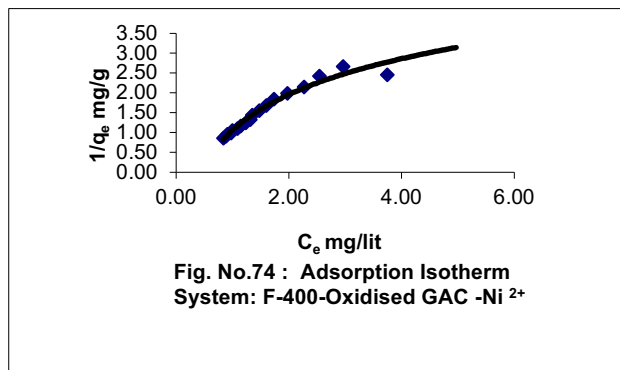
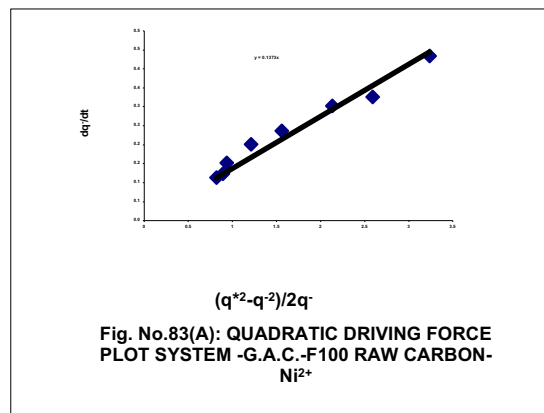
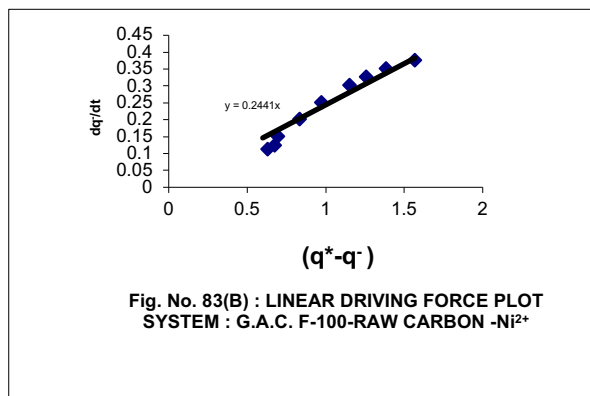
6	1.50	4.573	0.715	4.05	3.34	0.2010	11.1132
7	2.00	4.414	0.794	3.90	3.11	0.1873	9.1762
8	2.50	4.258	0.872	3.85	2.98	0.1567	8.0597
9	3.00	4.166	0.918	3.80	2.88	0.1369	7.4022
10	3.50	4.120	0.941	3.75	2.81	0.1221	6.9993
11	4.00	4.045	0.979	3.70	2.72	0.1102	6.5017



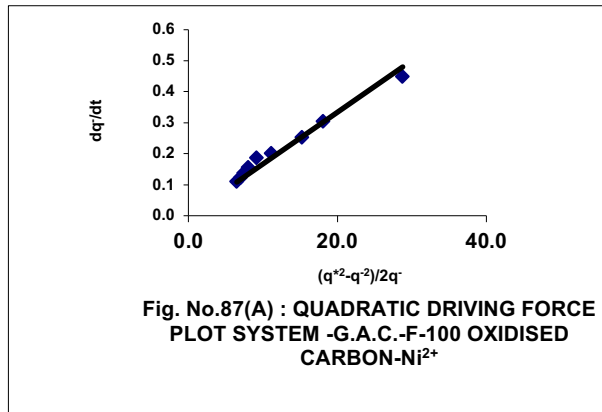
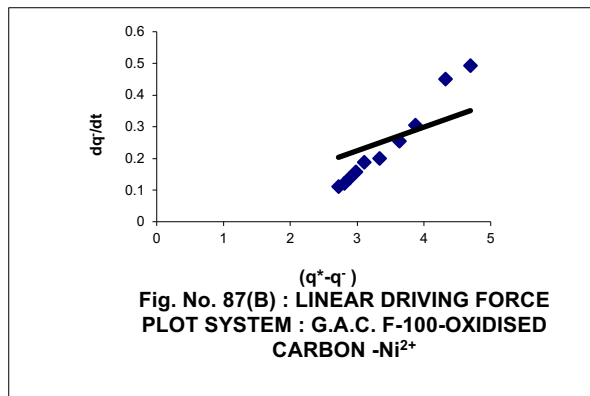
ADSORPTION PHASE APPROACH TO EQUILIBRIUM SYSTEM :

EQUILIBRIUM SYSTEM :

F-100-RAW CARBON- Ni²⁺



The use of GAC as an Adsorbent for the Removal of Heavy Metal Ions Ion from Aqueous solution using Batch Adsorption study.



Conclusion :

The batch adsorption study demonstrates that Granular Activated Carbon (GAC), especially chemically modified GAC using concentrated HNO₃, is a highly effective, low-cost adsorbent for removing heavy metal ions like Ni²⁺ from aqueous solutions. Key findings: High removal efficiency: Modified F-100 grade GAC showed significantly higher adsorption capacity for Ni²⁺ – 111.11 mg/g vs 45.45 mg/g for raw GAC. Surface area also increased from 1.51×10¹⁰ cm²/g to 3.296×10¹⁰ cm²/g after modification. Isotherm fit: The adsorption data for Ni²⁺ on both raw and oxidized GAC followed Langmuir and Freundlich models, confirming monolayer adsorption on a heterogeneous surface. Kinetics: The rate of Ni²⁺ uptake followed Linear Driving Force (LDF) and Quadratic Driving Force (QDF) models. Film diffusion effects were negligible at 1000 rpm, indicating that intraparticle diffusion was the rate-controlling step. Optimum conditions: Equilibrium was achieved within 6 hours at 28 ± 0.1°C. Stirring speed of 1000 rpm eliminated external film resistance. Recovery potential: Adsorbed metals can be recovered from GAC by leaching with concentrated HNO₃, making the process sustainable. Overall significance: Compared to conventional methods like chemical precipitation, ion exchange, and reverse osmosis, adsorption using GAC is simple, economical, and effective even at trace metal concentrations. Nitric acid modification enhances surface functional groups, increasing adsorption sites. This makes GAC, particularly Filtrasorb F-100, a practical adsorbent for treating industrial wastewater contaminated with toxic heavy metals. Future scope: GAC derived from agricultural waste or industrial byproducts can further reduce cost, making large-scale wastewater treatment viable.

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