

# Cobalt and Nickel Adsorption on Coal based Granular Activated Carbon F-200 & F100

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**Abstract – In this work the adsorption isotherm, Kinetic describes the adsorption of  $\text{Co}^{2+}$  &  $\text{Ni}^{2+}$  metal ions from aqueous solutions by F-300 Granular Activated carbon were studied. In all experimental system, concentration of solution, contact time, rpm and temperature were studied. The experimental data correlated well by the Langmuir and Freundlich adsorption isotherms and their constants were calculated. Cobalt adsorption using GAC F-200 & F-100 is very rapid in the first hour of contact where maximum metal ions are removed by GAC followed by a slow approach to equilibrium.**

**Index Terms – Adsorption, Cobalt, Nickel Granular Activated Carbon (GAC) GAC F-200 & F-100.**

## 1. INTRODUCTION

The pollution of water by heavy metals is becoming a serious global problem, as they are toxic, non-degradable, and bioaccumulative [1,2,3]. The fast development of industries such as metal plating, mining, fertilizers, tanneries, batteries, paper, pesticides, electronics, petro-chemical, textile, among others has contributed to an increase in the concentration of toxic metals in wastewaters which are directly or indirectly discharged into the environment, mainly in developing countries [3,4,5]. Also by a rapid increase in global industrial activities, pollution of water derived from the uncontrolled escape of heavy metals such as Copper, Nickel, Chromium, zinc and Cobalt has become serious.

Heavy metal contamination exists in aqueous wastes of many industries, such as plating, mining operations, tanneries, smelting alloy industries and storage batteries industries etc. These heavy metals have harmful effect on human physiology and other biological systems when they exceed the tolerance levels. Metals The inorganic micro pollutants, can be distinguished from other toxic 1046 pollutants, since they are not biodegradable, highly toxic [6,7]. These metals accumulated in living tissues, causing various diseases and disorders.

These metals are toxic in both their chemically combined forms as well as the elemental form. Cobalt is a hard ferromagnetic, silver-white, lustrous, brittle element. 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. However, too high concentrations of cobalt and Nickel may damage human health. Breathing in too high concentrations of cobalt through air, experience lung effects, such as asthma and

pneumonia. High concentration of cobalt is responsible for vomiting, nausea vision problems, heart problems and thyroid damage [8,9]. Therefore, toxic metals must be removed from wastewaters and acid mine drains in order to protect the environment and living organisms [3,10] various methods are being used to remove toxic metals. They include chemical precipitation, ion-exchange, adsorption, ultra- and nanofiltration, reverse osmosis, electrochemical, and electrodialysis techniques. Among these methods, adsorption has been recognized as an effective and economic method to treat waste waters containing toxic metals.

It offers flexibility in design and operation, as the adsorption process can be operated in batch or semi continuous (fixed-bed column) modes [3]. In general, adsorption also produces high-quality treated effluents and, because adsorption is often reversible, the adsorbents can be regenerated through a suitable desorption process and reused, and the adsorbate can also be recovered. When the adsorbent is reused and the adsorbate can be recovered, the adsorption is more economically favorable. [3] GAC adsorption can be selective, cheap and relatively inert and the high surface area along with the ability to chemically regenerate and reuse makes it very useful.

Among various treatment technologies, activated carbon adsorption is commonly used because it was shown to be economically favorable (compared with ion exchange, liquid extraction or electro dialysis), technically easy (compared with precipitation or reverse osmosis) and improved the efficiency of metallurgical carbon product in the removal of heavy metal from the synthetic wastewater, and it was divided into two parts. The first part consisted of characterization of physicochemical properties of activated carbon used in this work. The second part was an experimental study of adsorption of metal ion by activated carbon.

The study of adsorption kinetics is significant as it provides valuable insights into the reaction pathways and the mechanism of the reactions. Several kinetic models are used to explain the mechanism of the adsorption processes. Therefore, it is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to design appropriate adsorption treatment plants.

Granular Activated Carbon is widely used for the removal and recovery of toxic metals because of its low cost and high

affinity towards the metal ions. Activated carbon is the collective name for a group of porous carbons manufactured by the treatment of a char with oxidizing gases or by carbonization of carbonaceous *Adsorption of Cobalt onto Coal based Granular Activated Carbon*. All these carbons exhibit a high degree of porosity and an extended internal surface area. A number of adsorbents have been used by several workers for adsorbing toxic metals from their aqueous solutions. [11-19].

The influences of contact time of the solution, and initial metal-ion concentration on adsorption were also studied in detail. A suitable desorption process and the reuse of the spent adsorbent were also evaluated.

## 2. MATERIALS AND METHODS

### 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).

### 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.

### Glasswares:

All glasswares in laboratory were standard glass wares obtained from M/s Borosil, Bombay. Before use these glass wares were thoroughly washed with chromic acid & several times with distilled water & dried in oven.

### Electric Oven:

In this laboratory NEOLAB electric oven was used which had an arrangement to regulate the temperature to the required value.

### 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.

### 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.

### 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.

### 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 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.

## 3. APPARATUS

All absorbance measurements are taken by Digital Spectrophotometer (Type-166, Systronics India Ltd.) with matched cells of 1 cm optical path length.

### Reagents and Chemicals

Variety of carbon of Calgon Corporation Filtrasorb used namely F-100 Pittsburg (USA). All the reagents and chemicals used are of A.R. Grade. Cupric Sulphate (E. Merck India Ltd.) was used for the preparation of standard copper solution and it was diluted proportionately to prepare the experimental solution. Nitroso-R-Salt, sodium acetate solution used in the experiment were of Analytical Grade  $\text{HNO}_3$  from E. Merck India Ltd. was also used for oxidizing the carbon surface.

## 1) Surface area

Estimation of the specific surface area of granular activated carbon are based upon measurement of the capacity of the adsorbent expressed in mol/gm of GAC and related to the surface area using Langmuir equation for monomolecular adsorption. The relation relates the surface area to the monolayer capacity factor by the relation:

$$S = N_a \cdot Q^\circ \cdot A$$

Where,  $S$  = Surface area of the adsorbent in  $\text{m}^2/\text{g}$ ;  $N_a$  = Avagadro's number;

$Q^\circ$  = amount adsorbed per unit weight of the adsorbent forming a complex monolayer on the adsorbent surface in  $\text{mg/g}$ ;  $A$  = Cross sectional area of the adsorbate molecule in  $\text{m}^2$ .

Since the values of  $Q^\circ$  can be obtained from Langmuir plots of  $1/q_e$  versus  $1/C_e$ , the value of  $S$  for any particular GAC sample can be calculated. Here,  $q_e$  is the concentration of metal ion on GAC in  $\text{mg/g}$  of Carbon and  $C_e$  is equilibrium concentration of adsorbate in solution in  $\text{mg/L}$ . The occupied surface area of adsorbent by Copper ion due is calculated from the following expression

$$A = 4 \times 0.866 [M / (4\sqrt{2} \cdot N_a \cdot d)]^{2/3}$$

Where,  $M$  = Atomic weight of Copper I,  $N_a$  = The Avagadro number,  $d$  = the density of Copper Using  $M = 58.70$ ,  $N_a = 6.023 \times 10^{23}$  and  $d = 9.0$

## D) Preparation of the Co ion solution and its estimation.

In the present work solution of Cobalt ions was obtained using a solution of Cobalt Sulphate, which was prepared by dissolving Cobalt sulphate (Loba make) in distilled water and the cobalt ion content standardized by EDTA titrating using Xylenol orange indicator. 2ml of approximately 0.01 M Cobalt solution was diluted to 50 ml with distilled water and sufficient quantity of sulphuric acid was added to obtain a color change from red to yellow by addition of powdered hexamine to obtain a basic medium. The titration with standard EDTA was continued until a color changes from red to yellow was obtained [20].

The cobalt solution thus standardized was taken as a standard for preparation of Beer's law plot, which was more convenient and utilized in the present work to estimate Cobalt ions in all experimental solutions. Beer's Law for  $\text{Co}^{2+}$  was established spectrophotometrically. For this purpose 0.01M Cobalt solution was first prepared 10 ml of this solution was diluted to 1000ml in a clean volumetric flask. 1ml to 12 ml of diluted Cobalt ion solution was taken in several beakers. 2ml of 0.2% Nitroso-R-Salt solution was added to each beaker. The solution was heated and 1ml of 50% sodium acetate solution was added. The solution was boiled for 2 minutes and 2ml of 1:1  $\text{HNO}_3$  was added to each beaker. The volume of each beaker was then

diluted to 50 ml and absorbance was measured 425 nm spectrophotometrically using the Systronics Spectrophotometer Model No. 166 using 1 cm glass cuvettes against blank prepared similarly but without the Cobalt ion [21].

## 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  $\text{NH}_4\text{Cl}$  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 [22]. Working standard solutions were prepared by appropriate dilution of stock solution as in case 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 some time 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 [23]. 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.

## 4. RESULT &amp; DISCUSSION

## ADSORPTION ISOTHERM OF COBALT &amp; NICKEL METAL ION ON RAW GAC.

The adsorption isotherms of metal ions like Ni, Co on F-200 and F-100 grade of raw GAC is mentioned. These results are summarized in Tables 1 & 2 and Fig.1,2,3,4. These Figures at equilibrium show a plot of solid phase concentration of metal ions ( $\text{mg/gm}$ ) versus the equilibrium concentration of metal ions in solution ( $\text{mg/lit}$ ). 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.

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

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.

$W$  = Weight of carbon taken in grams.

Several types of isothermal adsorption relations may occur, the most common being the case where the adsorption leads to the deposition of an apparent single layer of adsorbate molecule on the surface of the adsorbent. The Langmuir adsorption while for multimolecular adsorption more complex adsorption models are to be considered.

The Langmuir treatment is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface that the energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface.

Using the values of  $q_e$  and  $C_e$  the Langmuir equation could be expressed as follows [4]

$$q_e = \frac{Q^\circ \cdot b \cdot C_e}{1 + b \cdot C_e}$$

Where  $Q^\circ$  = amount adsorbed per unit weight of the adsorbent forming a monolayer on the adsorbent surface in mg/gm.

$C_e$  = equilibrium concentration of adsorbate in solution in mg./lit.

$Q_e$  = amount of adsorbate adsorbed per unit weight of adsorbent in mg/gm.

$b$  = Langmuir constant

Rearranging the above expression

$$1/q_e = 1/(Q^\circ \cdot b \cdot C_e) + 1/Q^\circ$$

A plot of  $1/q_e$  versus  $1/C_e$  should be linear if Langmuir adsorption were Permitted calculation of  $Q^\circ$ . The value of  $Q^\circ$  being known, the surface area of the adsorbent could be determined. However, it must be cautioned that the Langmuir equation may not be strictly valid over the range of

concentrations used in the present work and only a mathematical analysis of the experimental data would substantiate this point.

The Langmuir equations for these systems also help in determining the surface area of the adsorbent under the present experimental conditions. Estimation of the specific surface area of GAC are based upon measurement of the capacity of the adsorbent expressed in mol/gm of GAC and related to the surface area using either the Langmuir equation for monomolecular adsorption or the B.E.T equation for multimolecular adsorption. The relation relates the surface area to the monolayer capacity factor by the relation:

$$S = N_a \cdot Q^\circ \cdot A$$

Where,

$S$  = Surface area of the adsorbent in  $m^2/gm$

$N_a$  = Avagadro's number

$A$  = Cross sectional area of the adsorbate molecule in  $m^2$ .

Since the values of  $Q^\circ$  can be obtained from Langmuir plots of data, it is possible to calculate the value of  $S$  for any particular GAC sample.

The Freundlich equation in an empirical equation and is often used as means of data description and generally agrees quite well with the Langmuir equation in a large number of cases. It is used for adsorption of gases and has been extended to dissolved solute over moderate to low concentrations of adsorbates.

$$\text{The equation is } q_e = K C_e^B$$

Where  $q_e$  and  $C_e$  have the same significance as mentioned before and  $k$  and  $\beta$  are Freundlich constants.

This relation is indicative of the adsorption capacity and intensity. It is verified by using the relation in the form.

$$\log q_e = \log k + \beta \log C_e$$

Determination of adsorption isotherm of Nickel on different on F200 & F-100 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  $28^\circ C$ . 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 nickel ion on GAC in mg/gm of carbon

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

$C_e$  = Equilibrium concentration of nickel ions in solution in mg Per liter.

$V$  = Volume of solution taken in liters.

$W$  = Weight of carbon taken in grams.

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 1, as also  $\log q_e$ ,  $\log C_e$  and  $1/q_e$  and  $1/C_e$  values for which are useful test for adherence of adsorption of chromium ions to either the Freundlich or the Langmuir adsorption models. The isotherms and the adherence to Freundlich and Langmuir theories.

Similar procedure was also followed for determining the adsorption isotherms of the Cobalt ions.

Table-1

Sr No	Metal ions	Grades of raw GAC	$q_{\text{emax}}$ mg/gm
1	$\text{Co}^{2+}$	F-200	1.089
2	$\text{Ni}^{2+}$	F-200	3.105

From this Table it is observed that the order of adsorption follows the trend

$$F-400 > F-300 > F-200 > F-100$$

The Langmuir equation of a plot of  $1/q_e$  versus  $1/C_e$  for  $\text{Ni}^{2+}$  ions adsorption could further throws more light on the surface area occupied by the Nickel ion on the GAC.

In utilizing the expression

$$S = Q_o \cdot N_a \cdot A$$

Determination of value of  $S$  needed the determination of  $A$  the surface area occupied by a single Nickel ion due to the adsorption of the Nickel metal ions by GAC. The expression used by Brunauer and Emmett [5]

$$A = 4 \times 0.866 \left[ \frac{M}{4\sqrt{2} \cdot N_a \cdot d} \right]^{2/3}$$

Where  $M$  = Atomic weight of nickel

$N_a$  = The Avagadro number

$d$  = the density of Nickel

Using  $M = 58.70$ ,  $N_a = 6.023 \times 10^{23}$  and  $d = 9.0$  [6]

For other metal ions like  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  the surface area for raw GAC can be calculated same as above procedure. Above equation was also followed for the surface area of the same metal ion for oxidized GAC and also for mixture of the metal ion solution.

Atomic weight and density of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  given as follows.

For  $\text{Co}^{2+}$  metal ion

$$A=58.90$$

$$N_a = 6.023 \times 10^{23}$$

$$d = 8.83$$

For  $\text{Cu}^{2+}$  metal ion

$$A=63.5$$

$$N_a = 6.023 \times 10^{23}$$

$$d = 8.92$$

For  $\text{Ni}^{2+}$  &  $\text{Co}^{2+}$  metal ion

$$A=51.99$$

$$N_a = 6.023 \times 10^{23}$$

$$d = 7.19$$

The values of  $A$  and  $S$  are reported in the following Table 2 –

Sr. No.	Metal ion	Grades of raw GAC	$Q^o$ g/mg	$A$ $10^{-16} \text{cm}^2$	$S$ $\text{cm}^2/\text{gm}$	$S'$ $\text{cm}^2/\text{gm}$
1	$\text{Co}^{2+}$	F-200	19.2307	5.322	$6.163 \times 10^{10}$	$5.927 \times 10^{10}$
2	$\text{Co}^{2+}$	F-100	15.3846	5.322	$4.931 \times 10^{10}$	$5.725 \times 10^{10}$

3	Ni <sup>2+</sup>	F-200	55.5555	5.244	1.755 x10 <sup>10</sup>	1.67 x 10 <sup>10</sup>
4	Ni <sup>2+</sup>	F-100	45.4545	5.244	1.436 x10 <sup>10</sup>	1.51 x10 <sup>10</sup>

A glance of the Table clearly indicates that the surface area occupied by the different metal ions on the surface follows the same trend as for  $q_{\text{emax}}$  values i.e.

$$F-200 > F-100$$

However the values of the area occupied by Nickel on the GAC when the surface is saturated with a monolayer of Nickel ion could be roughly assessed by utilizing the values of  $q_{\text{emax}}$  in mg per gm of carbon and converting it into atoms per gm of carbon by the relation.

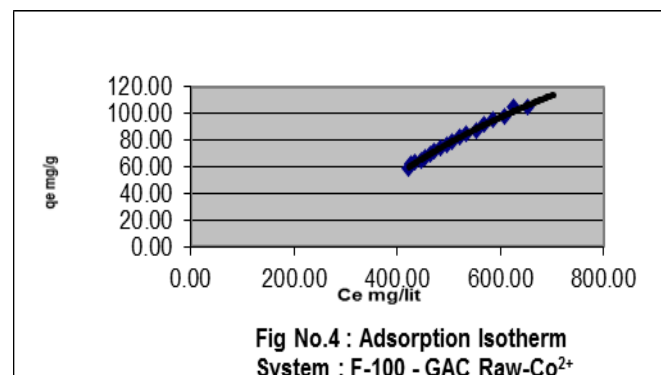
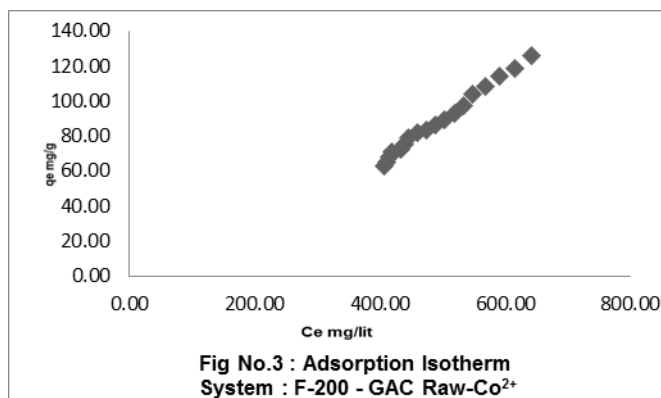
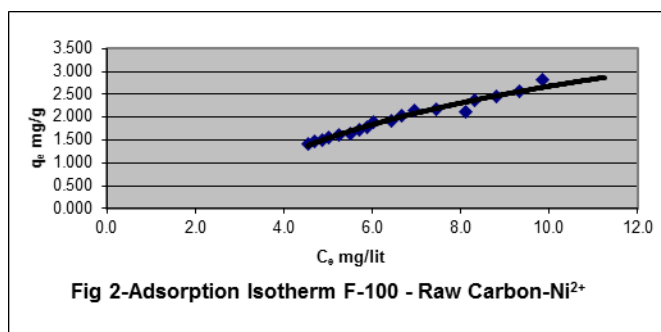
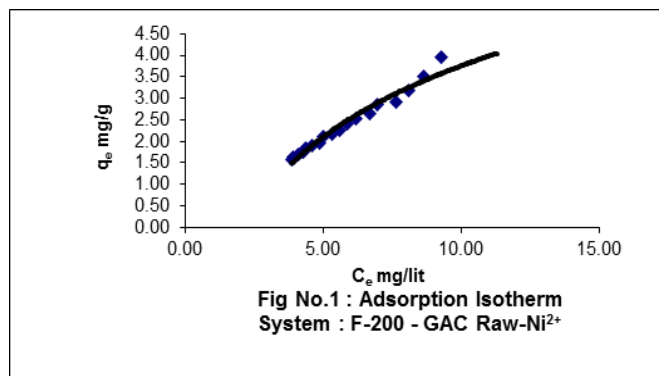
$$\frac{(q_{\text{emax}}) \times 6.023 \times 10^{23}}{1000 \times 58.70}$$

Multiplication of this with the surface area of a single Nickel ion, A, i.e.  $5.244 \times 10^{-16}$  would give the actual area occupied by the Nickel adsorbed on the surface. The surface area occupied by Nickel follows a trend.

$$F-200 > F-100$$

In Table B,  $Q^0$  value were obtained by the reciprocal of the intercept, from a plot of  $1/q_e$  versus  $1/C_e = 0$ . Since this value is in mg/gm of carbon it was converted to atoms per gram of carbon by the above mentioned relation which afforded surface area to be calculated as shown under S. Value of  $S'$  in the same Table occupied by Nickel ion forming a monolayer on the surface obtained from  $q_{\text{emax}}$  values is calculated using  $q_{\text{emax}}$  converted to atoms per gram by dividing by 5870 (i.e. At. Wt. of Ni in mg) and using values  $N_a$  and  $A$  as above get  $S'$ .

The close comparison of  $S$  and  $S'$  substantiates our reasoning. It justifies the reason of carbon adsorption is utilized as a tertiary treatment step in all wastewater treatment processes.



## 5. CONCLUSION

On the basis of this study it is concluded that GAC F-200 & F-100 has good potential as a cheap and effective scavenger for  $\text{Co}^{2+}$  &  $\text{Ni}^{2+}$  present in aqueous solutions and can be effectively utilized for waste water treatment. The present study demonstrated that Granular Activated Carbon can be used efficiently in the removal of Cobalt & Nickel from aqueous solution. The uptake of Cobalt & Nickel on F-200 GAC was found to be good. The adsorption isotherms obtained from the present work may be helpful in designing industrial adsorption columns.

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