Adsorption study on F-400 Modified Granular Activated Carbon for the different ratio of Cr: Ni & Ni:Cr metal ions.

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ABSTRACT

Activated carbon was used to remove Ni (II) from aqueous solution by adsorption. Batch adsorption studies were carried out by varying the contact time, initial Ni (II) ion & $Cr_2O_7^{2-}$ concentration in the aqueous solution, adsorbent dosage, and temperature. Maximum adsorption was observed with contact time of 6 hrs, adsorbent dosage of 0.1 to 1gm and at the temperature of 28^0 C. It was indicated from the results that the effective removal of Ni^{2+} and $Cr_2O_7^{2-}$ by modified Granular Activated Carbon.
The adsorption isotherms were obtained in a batch reactor. It is observed that, the process of uptake followed first-order adsorption rate expression and obeyed Langmuir and Freundlich models of adsorption. Effects of variations in parameters such as contact time, adsorbent dose, initial Ni(II) concentration and particle size were also studied.

KEYWORDS: Nickel (II), $Cr_2O_7^{2-}$ removal, Activated carbon, Adsorption isotherm.

I. INTRODUCTION

The presence of heavy metals in the environment can be detrimental to the living species. Despite strict environmental regulations, significant quantities of heavy metals are found in the wastewaters from several industries such as non ferrous metal, electroplating, porcelain enameling, silver refining, welding, alloy manufacturing and fertilizer industry.

Heavy metals have been used extensively in electroplating and metal surface treatment processes generate significant quantities of wastewater containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver and titanium) from a variety of applications. Therefore, it is necessary to treat metal contaminate wastewater prior to its discharge to the environment [1]. Various treatments technologies have been developed successfully for purification of contaminated water and wastewater from heavy metals [2].

The heavy metals are trace metals with density at least five times that of water. They are Table- elements and are bioaccumulative in their nature. They include mercury, nickel, lead, arsenic,cadmium, chromium, aluminium, platinum, zinc, silver and gold [3]. Nickel is highly toxic and is present in the waste waters of industries such as paper and pulp, fertilizer, silver refining, pigments and coatings, basic steel work foundry, automobile, petroleum refining[4].

The most likely sources of nickel emissions are found to be from metallurgical plants [5], engines burning fuel containing nickel additives, plating plants [6], and incineration of nickel products, metal extraction, fabrication operation and effluent from nickel cadmium battery industries [7].The target tissues affected by nickel include skin, larynx, nasal passages and lungs. The signs and symptoms of nickel exposure include blue colored lips, cancer of lungs, nasal cavity and larynx, contact dermatitis, fever, headache, dizziness, skin rashes and vomiting (8). The incidence of lung and nasopharyngeal cancer in occupationally exposed population is due to the carcinogenic effect of nickel [9].Various treatments technologies have been developed successfully for purification of contaminated water and wastewater from heavy metals [10].

The most commonly used methods for the removal of metal ions from industrial effluents include chemical precipitation, solvent extraction, reverse osmosis, membrane filtration, electro deposition, ion exchange and adsorption on to low-cost materials [11-14]. Adsorption is one of the easiest, safest, and less cost effective methods because it is widely used in effluent treatment processes [15, 16]. However, adsorption by activated carbon had been reported as a technically and economically viable technology for heavy metal removal [17 Typically, the preparation of activated carbon can be divided into two processes [18].First, the physical method consists of the pyrolysis of the precursor material and gasification of the resulting char in steam or carbon dioxide [19, 20].. Second, from the chemical method which pyrolysis char would be impregnated with acids, strong bases or other chemicals [21].. In this work, investigation on the effect of initial concentration, adsorbent dosage, particle size, pH and temperature on metal adsorption from aqueous solution was carried out using leaves of bitter orange based activated carbon.

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. Hydrabad , 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° ± 0.1°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° ± 0.1°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.

<center>**Apparatus**</center>

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

THE SELECTION OF ADSORBENTS AND THEIR CHARACTERIZATION.

In the present work the selection of F-400, F-300, F-200, F-100 Granular Activated Carbon was used in certain isotherm and kinetic studies because they were readily available in the laboratory. M/s. Calgon Corporation, Pittsburg, and U.S.A supplied these. These grades of carbon are common grades and find extensive use in the studies of adsorption of organics and inorganic in literature.

<center>**Reagents and Chemicals**</center>

Various varieties of carbons of Corporation Filtrasorb used namely F-100, F200, F300 & F400 LCK, RRL, Lurgi (German). All the reagents and chemicals used are of A.R. Grade. hydrated cupric chloride (E. Merck India Ltd.) was used for the preparation of standard nickel solution and it was diluted proportionately to prepare the experimental solution., HCl, dilute ammonia solution, Mureoxide indicator, buffer solution (citric acid + liquid ammonia) of the pH = 8.5, sodium diethyldithio carbamate solution, chloroform, anhydrous sodium sulphate used in the experiment were of Analytical Grade HNO_3 from E. Merck India Ltd. was also used for oxidizing the carbon surface.

<center>**Surface area**</center>

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:

$$S = N_a.Q^o.A$$

Where, S = Surface area of the adsorbent in m^2/g;

N_a = Avagadro's number;

Q^o = amount adsorbed per unit weight of the adsorbent forming a complex monolayer on the adsorbent surface in mg/g;

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

Since the values of Q^o 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 mg/g of Carbon and C_e is equilibrium concentration of adsorbate in solution in mg/L. The occupied surface area of adsorbent by Nickel ion due is calculated from the following expression

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

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

Adsorption experiments

For determining the adsorption isotherm of nickel ion on granular activated carbon like F-400, varying weight of GAC was taken into a 1 liter Round Bottom Flask and placed carefully in thermostat for each set of experiment. A fixed concentration of 200 ml 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. Aliquots of 5 ml of nickel ion solution were then withdrawn from the flask and analysed calorimetrically for nickel ion concentration. 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.

$$q_e = (Co – C_e) \times \quad V/W$$

Where, q_e = Concentration of nickel ion on GAC in mg/g of carbon;

C_o = Initial concentration of nickel ions in solution in mg/l;

C_e = Equilibrium concentration of nickel ions in solution in mg/L;

V = Volume of solution taken in liters; W = Weight of carbon taken in g.

Adsorption Isotherm of Nickel on Different Grades of GAC

A set of twenty points of equilibrium concentration of Nickel was adsorbed on GAC in different experimental setups. The concentration of Nickel ion on GAC in mg/g of carbon was calculated by using following expression

$$qe = (C_0-Ce) \times V/W$$

where, qe = Concentration of Nickel ion on GAC in mg/g of carbon;

C_0 = Initial concentration of Nickel ion in solution in mg dm^{-3};

Ce = Equilibrium concentration of Nickel ion in solution in mg dm^{-3};

V = Volume of solution taken in liters;

W = Weight of the carbon taken in g.

(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 colour of the solution turned yellow. It was then titrated against a standard 0.01M EDTA solution when the colour 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.

Preparation of solution of Chromium ion and its estimation.

A standard chromium ion stock solution was prepared by dissolving 0.2941 gm of potassium Dichromate (E. Merck India Ltd.) in 100ml-distilled water. The chromium solution used for the preparation of standard Beer's Law discussed above was estimated with AAS at RSIC, Nagpur and was found to be 1ml = 3.119 mg of chromium. Working solutions were prepared by appropriate dilution of the above standard stock solution. For the preparation of the standard Beer's Law plot, chromium solutions were taken in the concentration range of about 10^{-5} M. Various aliquots of the chromium solution of the above concentration were taken in different small conical flasks. 2ml of 3M sulphuric acid was added to it. The total volume of the solution was kept to 20 ml by adding distilled water to it. Then 1ml of 1,5 –diphenyl carbazide solution in 50 % acetone was added when a violet color developed. The absorbance of the solution was measured at 540nm against a reagent blank [24]. The reagent blank contained all above solutions added except chromium ion solution. A graph of absorbance versus concentration of the chromium ion gave a straight-line fit and regression analysis of data was carried out to obtain a working equation was used in all calculations. The Beer's Law data and the working equation are given in **Table**

III) 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-400 GAC or different grades like F-100, F-200, or F-300 of carbon was treated with concentrated HNO_3 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-400.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 qe 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 / liter.

V = Volume of solution taken in liters.

W = Weight of carbon taken in grams.

TABLE 1

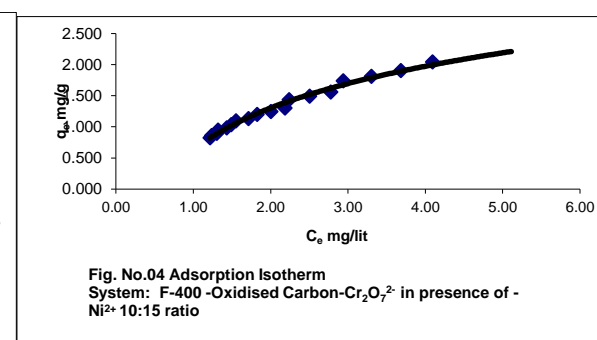| Sr No	Metal ions	Concentration of Metal ions	Grades of Modified GAC	q_{emax} for nickel in mg/gm
1	Cr:Ni	10:10	F-400	2.762
2	Cr:Ni	10:13	F-400	4.006
3	Cr:Ni	10:16	F-400	4.494
4	Cr:Ni	10:20	F-400	4.885
5	Ni:Cr	10:13	F-400	1.983
6	Ni:Cr	10:16	F-400	1.551
7	NiCr	10:20	F-400	1.474

TABLE 2

Sr. No.	Metal ion	Grades of modified GAC	Concentration of metal ions	Q^o g/mg for nickel	A 10^{-6} cm^2	S cm^2/gm for nickel	S' cm^2/gm for nickel
1	Cr:Ni	F-400	10:10	50.0000	5.244	1.579×10^{10}	1.486×10^{10}
2	Cr:Ni	F-400	10:13	71.4286	5.244	2.256×10^{10}	2.156×10^{10}
3	Cr:Ni	F-400	10:16	83.3333	5.244	2.632×10^{10}	2.418×10^{10}
4	Cr:Ni	F-400	10:20	90.9090	5.244	2.871×10^{10}	2.626×10^{10}
5	Ni:Cr	F-400	10:13	33.0033	5.244	1.042×10^{10}	1.067×10^{10}
6	Ni:Cr	F-400	10:16	25.0000	5.244	7.896×10^{10}	8.345×10^{10}
7	NiCr	F-400	10:20	21.7391	5.244	6.866×10^{10}	7.931×10^{10}

TABLE 3

Sr No	Metal ions	Concentration of Metal ions	Grades of Modified GAC	q_{emax} for Chromium in mg/gm
1	Ni:Cr	10:10	F-400	2.319
2	Ni:Cr	10:13	F-400	2.986
3	Ni:Cr	10:16	F-400	3.662
4	Ni:Cr	10:20	F-400	4.112
5	Cr:Ni	10:13	F-400	2.142
6	Cr:Ni	10:16	F-400	0.193
7	Cr:Ni	10:20	F-400	0.224

TABLE 4

Sr. No.	Metal ion	Grades of modified GAC	Concentration of metal ions	Q^o g/mg for Cr	A $10^{-6}cm^2$	S cm^2/gm for Cr	S′ cm^2/gm for Cr
1	Cr:Ni	F-400	10:10	58.8235	5.244	1.858×10^{10}	1.248×10^{10}
2	Cr:Ni	F-400	10:13	33.3333	5.244	1.053×10^{10}	1.153×10^{10}
3	Cr:Ni	F-400	10:16	5.17330	5.244	1.634×10^{10}	1.040×10^{10}
4	Cr:Ni	F-400	10:20	4.46030	5.244	2.632×10^{10}	1.206×10^{10}
5	Ni:Cr	F-400	10:13	62.5000	5.244	1.974×10^{10}	1.607×10^{10}
6	Ni:Cr	F-400	10:16	66.6666	5.244	2.106×10^{10}	1.970×10^{10}
7	Ni:Cr	F-400	10:20	83.3333	5.244	2.632×10^{10}	2.213×10^{10}

Fig. No 01.Adsorption Isotherm
System: F-400 -Oxidised GAC-Ni^{2+}in presence of Cr^{6+} 10:13 ratio

Fig. No.02 Adsorption Isotherm
System: F-400 -Oxidised GAC-Ni^{2+}in presence of Cr^{6+} 10:15

Fig. No.03 Adsorption Isotherm
System: F-400 -Oxidised GAC -Cr$_2$O$_7^{2-}$ in presence of - Ni^{2+} 10:13 ratio

Fig. No.04 Adsorption Isotherm
System: F-400 -Oxidised Carbon-Cr$_2$O$_7^{2-}$ in presence of - Ni^{2+} 10:15 ratio
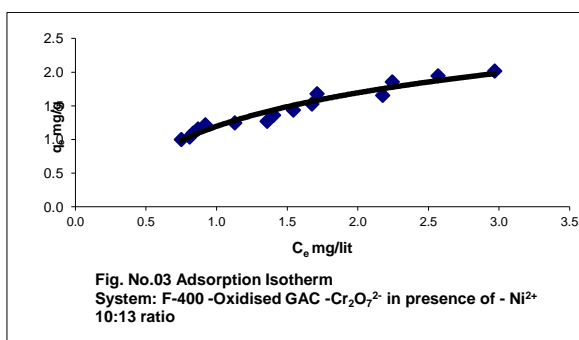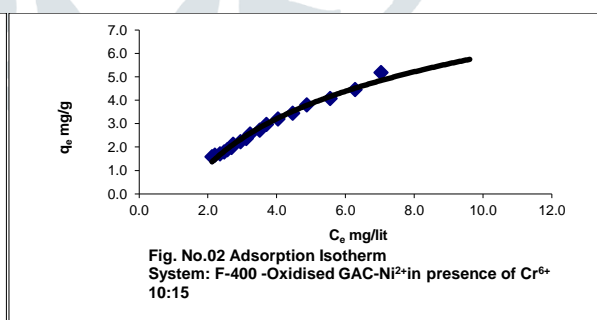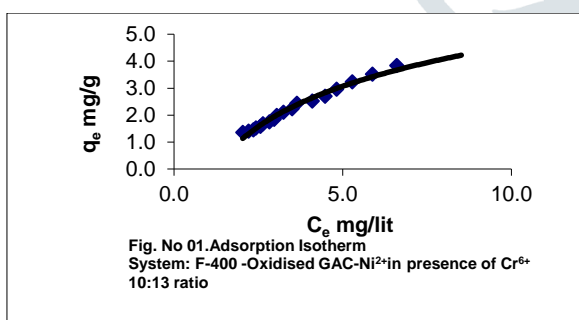
Result and Discussion

In the present study varying the concentration of nickel and taking the fixed concentration of chromium studied the adsorption isotherm of Cr and Ni by taking the proportion 10:10, 10:13, 10:16 and 10:20 of Cr:Ni respectively. The presence of chromium hinders the adsorption of nickel. q_{emax} and surface area of Cr and Ni was reported in table .When the concentration of nickel was constant and chromium was varied, by taking the concentration as 10:10, 10:13, 10:16 and 10:20 of Ni:Cr and Cr:Ni respectively, the presence of nickel hinders the adsorption of chromium. The surface area and the q_{emax} value were reported in table.

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