Adsorption and Kinetic studies on the removal of Co²⁺ and Ni²⁺ from aqueous solution by the use Granular Activated Carbon.

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Abstract

This paper presents the feasibility of removal of basic heavy metal ions Cobalt and Nickel from aqueous solutions by using a low cost Granular Activated Carbon F100, F200, F300, F400 GAC as an adsorbent. Batch adsorption experiments were carried out as a function of contact time, initial concentration of the adsorbate, adsorbent dosage and temperature. Effects of adsorbent concentration, agitation time and initial ion concentration on the adsorption behaviour are investigated and adsorption isotherm and kinetics on Granular Activated carbons are also studied. Heavy metal ions adsorption equilibrium was rapidly attained after 5 hours of the contact time, and it was described by the Langmuir and Freundlich adsorption isotherms over the entire concentration range.

Keywords – **F200 and F300 GAC, Isotherms and Kinetics**.

I. INTRODUCTION

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 enamelling, silver refining, welding, alloy manufacturing and fertilizer industry. The heavy metals are trace metals with density at least five times that of water. They are Table- elements and are bio accumulative in their nature. They include mercury, nickel, lead, arsenic, cadmium, chromium, aluminium, platinum, zinc, silver and gold (1Heavy metals are usually present in wastewaters which are released into the environment from various industries.**[1]** The adverse effects caused by these heavy metals are of great environmental concern. Heavy metals are non biodegradable and accumulate in living organisms thereby causing various diseases and disorders.**[2]** Cobalt, Chromium and nickel are frequently used in industrial processes such as metal plating industries, galvanizing industries, mining operations and tanneries and are usually present in high concentrations in the liquid wastes which are released directly into the environment without any pre-treatment. Once in the environment, chromium exists mainly in two oxidation states (Cr(III) and Cr(VI)). While Cr(III) is relatively innocuous, Cr(VI) is toxic, carcinogenic and mutagenic. It is highly mobile in soil and aquatic system and is a strong oxidant capable of being adsorbed by the skin **[3]** Nickel toxicity has been known to inhibit spermatogenesis, amylase enzymes, insulin formation and kidney formation. Due to the high toxicity of these metals, there is increasing interest in the development of techniques for their removal from wastewaters before they are disposed into the environment. Some of the techniques which have been used in the removal of metals from effluents include ion-exchange, chemical precipitation, electro dialysis, electrolytic extraction, reverse osmosis and cementation. These methods are expensive and have the inability to remove metals at low concentration **[4]** Among these methods, carbon adsorption is the most attractive one because of its efficiency, economical feasibility and the ease for the treatment of wastewater containing lead ions. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration **[5]** Some studies on the use of adsorbent such as sawdust and teak tree bark, waste tea, coconut shell and dry plants on the removal of metals from aqueous solutions have been reported **[6]** The adsorption capacities of these materials have been shown to be dependent on experimental conditions such as, metal concentration and adsorbent loading. The aim of this research is to investigate the use of modified coconut husk in the removal of metals from aqueous solutions.

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

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.

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:

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

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

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

Where, M = Atomic weight of nickel, Na = The Avagadro number, d = The density of Nickel Using M = 58.70, N_a = 6.023 x10^{23} and d = 9.0

Adsorption experiments

For determining the adsorption isotherm of nickel ion on different grades of grades of granular activated carbon like F-300, F-200 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.

$$q_e = (Co – C_e) \, x \quad V/W$$

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

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

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 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 [7]. 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 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 [8]. 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 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 cobaltion 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 [9].

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 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 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 [10].
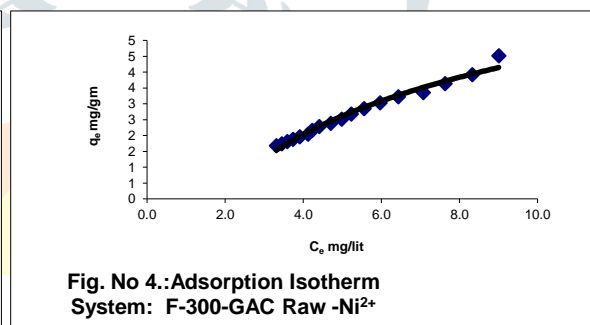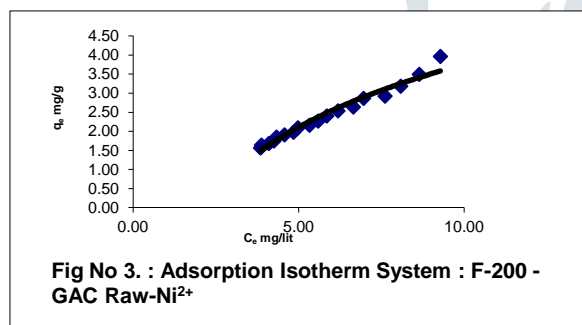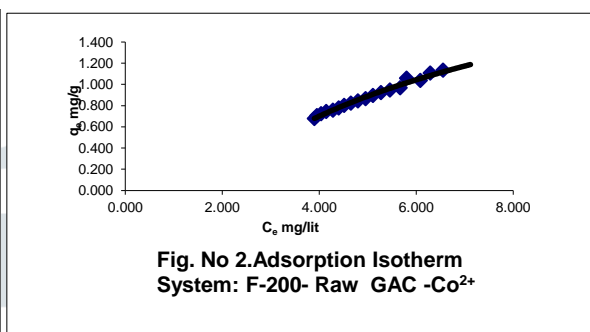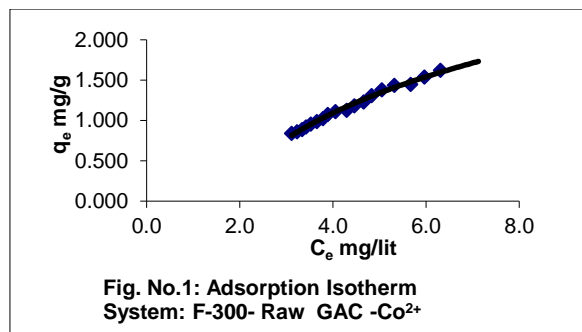

Fig. No.1: Adsorption Isotherm System: F-300- Raw GAC -Co^{2+}

Fig. No 2.Adsorption Isotherm System: F-200- Raw GAC -Co^{2+}

Fig No 3. : Adsorption Isotherm System : F-200 - GAC Raw-Ni^{2+}

Fig. No 4.:Adsorption Isotherm System: F-300-GAC Raw -Ni^{2+}

Table 1-

Sr. No.	Metal ion	Grades of raw GAC	Q^o g/mg	A $10^{-16}cm^2$	S cm^2/gm	S' cm^2/gm
1	Ni^{2+}	F-200	55.5555	5.244	1.755×10^{10}	1.67×10^{10}
2	Ni^{2+}	F-300	71.4285	5.244	2.256×10^{10}	2.13×10^{10}

Table-2

Sr. No.	Metal ion	Grades of modified GAC	Q^o g/mg	A $10^{-16}cm^2$	S cm^2/gm	S' cm^2/gm
1	Co^{2+}	F-200	19.2307	5.322	6.163×10^{10}	5.927×10^{10}
2	Co^{2+}	F-300	25.0000	5.322	8.013×10^{10}	9.785×10^{10}

(X) 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 namely.

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

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
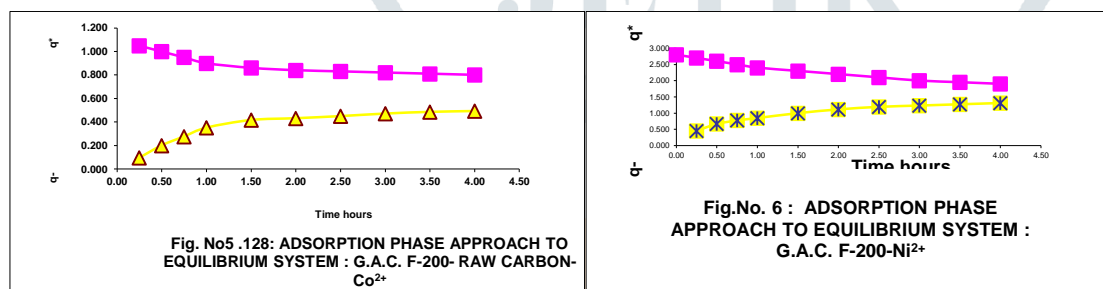
C_t = The concentration of the nickel ion in the solution at any time t

In mg/lit.

W = Weight of carbon taken in gm

V = Volume of nickel solution in liters.

The rate of adsorption of the nickel metal on different grades of carbon and data represents in Tables 1 & 2

Values of the q^- at different time intervals were then plotted versus these time intervals. q^{-*} 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^- at $C_e = C_t$ which was q^{-*}. A plot both q and q^* were plotted versus different time interval. These curves represents the approach to equilibrium **Figure 5 & 6** .The difference between the values of q^{-*} and q^- 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^{-*} and q^- are given in above Tables for the two grades of Raw Granular Activated Carbon and oxidized Granular Activated Carbon. These Tables also give calculated values of dq^-/d_t 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. Discussion about this in Chapter IV.

Fig. No5 .128: ADSORPTION PHASE APPROACH TO EQUILIBRIUM SYSTEM : G.A.C. F-200- RAW CARBON- Co^{2+}

Fig.No. 6 : ADSORPTION PHASE APPROACH TO EQUILIBRIUM SYSTEM : G.A.C. F-200-Ni^{2+}

RESULT AND DISCUSSION

Characterization of Adsorbent

In the present work, two grades of carbon namely Filtrasorb F-300 & F-200 were used for isotherm and kinetic studies. The characteristic properties of all the grades of carbon are given in Table . It is observed that the surface areas of F-300 are slightly larger than those of F-200. A gradual decrease in the porosity observed from F-300 to F-200 carbon samples. Whereas the pore volume also follow same trend except that the pore volume of F-300 is higher than that of F-200.

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