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Recovery and Reuse of Adsorbed Heavy Metal Ions by Adsorption Technology

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Abstract **: The heavy metal is arising as the most harmful to both water sources and atmosphere quality. Adsorption method is widely used to remove heavy metal ions from waste water . Various industries are the major sources of discharging heavy metals. They can be toxic for nature and can cause severe problems for humans and aquatic ecosystem. Because of low cost of Granular activated carbon and easy availability adsorption process is widely used for the removal of heavy metals. To limit the spread of the heavy metals such as Nickel within water sources, Granular Activated Carbon F-400 is used as a adsorbents and also studied the recovery of same metal ion from GAC.**

Index Terms **: Adsorption, Aqueous Solution, GAC, Heavy metal, Nickel , Recovery.**

I. INTRODUCTION

Enlightening to heavy metals, at trace levels, is harmful to human beings (Jamil, 2010; Khan, 2008; Singh, 2010; Peng, 2004) .Thus, removal of undesirable metals from water sources is considered as an important task that is still threatening the environment. WHO recommended safe limits for Nickel in waste water are 0.02 ppm to 0.05 ppm..Exposure of humans to contaminated wastewater is often possible especially in urban highly populated areas or where the wastewater is reused for agricultural activities.(Chiroma,2014., Aneyo, 2016).Depending on the dose and length of exposure, as an immune toxic and carcinogen agent, Ni can cause a variety of health effects, such as contact dermatitis, cardiovascular disease, asthma, lung fibrosis, and respiratory tract cancer (Chen, 2017). Exposure by inhalation a main route for nickel-induced toxicity in the respiratory tract, in the lung, and immune system, it also affect, mainly those who handle stainless steel and nickel-plated articles, (Sinicropi, 2010). However, the exposure of human beings mainly concerns oral ingestion through water and food as nickel may be a contaminant in drinking water and/or food (Sinicropi, 2012). Thus, scavenging of undesirable metals from waste water sources is considered as an important task that is still harmful to the environment. (Geneva, 1998)

In this article, we have also studied effective reuse of adsorbed metal by recovery study. The high spread of products containing this metal unavoidably leads to pollution of the environment by nickel and its secondary products at all stages of manufacturing, recycling and disposal. in humans, Nickel has an important nutrient for some microorganisms, plants, and animal species (Muñoz, 2012). Nickel-based enzymes are well known in the, bacteria, algae, and plants (Ragsdale, 2013., Boer, 2014., Maroney, 2014, Desguin, 2018., Sawers 2017). Nickel alters the metabolic activities of the plants, photosynthetic electron transport and chlorophyll, biosynthesis (Sreekanth, 2013). Numerous methods are reported as efficient for the removal of and electrochemical technologies.(Wang, 2011; Wang, 2003; Connell, 2008; Kurniawan, 2006; Galil, 1990; Eid, 2005).

Out of these techniques, adsorption is the best technology to remove heavy metal ions. In addition, the reversible nature of most adsorption processes, adsorbents could be regenerated by suitable desorption processes for various use (Pan, 2009).

Because of low maintenance cost, high efficiency, and ease of operation this process is preferable. (Mishra, 1996). Therefore, the adsorption process is considered as one of the major suitable technique for heavy metals removal from water/wastewater sources.

This chapter highlighting methods employed and experimental techniques in studying the adsorption of metals as Ni^{2-} on F-400grades of Granular Activated Raw Carbon.(G.A.C.) and Granular Activated Oxidized Carbon carried out by batch experiment and fixed bed column studies.

II. MATERIALS AND METHODS

1) 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 used in laboratory from (M/s. Kumar, Industries Mumbai, Capacity 1.5 lit/hour). Distilled water thus obtained 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.
2) Glasswares **:** In laboratory all glass wares were standard obtained from Borosil, Bombay. These glasswares were thoroughly washed with chromic acid & several times with distilled water before using & dried in oven.
3) Electric Oven **:** In this laboratory NEOLAB electric oven was used which had an arrangement to regulate the temperature to the required value.
4) Balance **:** The balance used for weighing was a electronic balance with an accuracy .
5) Mechanical Shaker **:** A mechanical shaker was used for agitation of GAC with solution for some adsorption experiments. The shaker was useful for adsorbing the metals on Granular Activated Raw 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.
6) 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.
7) Thermostat Bath : A thermostat arrangement, which was an essential requirement for agitating the loaded carbon with metal ion solution,possible to run the thermostat continuously at the temperature of 28° ± 0.1°C during the entire work. Once all facilities were readily available it was possible to plan adsorption studies as also to carry out rate of adsorption in the present work.

Adsorbent Choice :

Activated carbon readily available in the laboratory were the Calgon Corporation Filtrasorb variety 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 this article we are mentioning work on F-400.

III. EXPERIMENTAL ARRANGEMENT AND METHOD FOR CARRYING OUT ADSORPTION STUDIES

To determine the adsorption isotherm of metal ions (Ni^{2+}) 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. Stirred the contents by using a paddle type glass stirrer with the help of Remi stirrers. 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 ± 0.5°C.

RB flask of 1 liter used for experiment with the tub bath and different weights of GAC (Granular Activated Carbon) drying weight of carbon from by 0.1 gm to 1 gm carbon. 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 speed 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 the following expression.

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

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.

IV. RESULT AND DISCUSSION

Determination of adsorption isotherm of Nickel on F-400 grades of granular activated carbon **:**

Adsorption isotherm of nickel ion on different grades of grades of granular activated carbon like F-400 varying weight of GAC was taken into a 1 liter round bottom flask carefully for each set of experiment helps to determine isotherms of adsorption. .Also take fixed concentration of 200ml of nickel ion in solution was then introduced. The stirrer was placed in position and stirred for six hours at 28°C. By spectrophotometrically the initial and final concentration of nickel ion in mg/lit was recorded by . By using following formula the value of both values C_o and C_e, the value of q_e, the amount of nickel adsorbed on the GAC.

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

Thus for each GAC- Chromium ion system there is available a set of data for q_e and C_e. Following graph q_e versus C_e then represents a typical adsorption isotherm for the nickel ion. In following table the data on these isotherm are, as also log q_e , log C_e and 1/qe and $1/C_e$ values for which are useful test for adherence of adsorption of Nickel ions to either the Freundlich or the Langmuir adsorption models. The isotherms also adherence to Freundlich and Langmuir theories .

Table I. q_{max} of Raw GAC F-400

Sr. No	Metal ions	Grade of raw GAC	q_{emax} mg/gm
1	Ni^{2+}	F-400	4.52

The Langmuir equation of a plot of $1/q_e$ versus $1/C_e$ for 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

$$S = Q_o . Na . A$$

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 (Kapoor,1988)

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

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 (Zogorskii,1974).

Table II. Surface Area of Raw GAC F-400 occupied by Ni2+ metal ion due to adsorption.

Sr. No.	Metal ion	Grades of raw GAC	Q^o g/mg	A 10^{-16} cm^2	S cm^2/gm
1	Ni^{2+}	F-400	83.33	5.24	44.83

Above table clearly indicates that, 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_{emax} in mg per gm of carbon and converting it into atoms per gm of carbon by the relation.

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

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

Fig. No. a

Adsorption Isotherm F-400 - Raw Carbon-Ni^{2+}

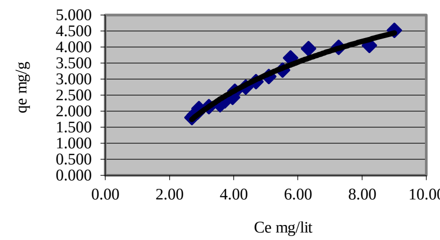

Fig. No. b

Linearised Freundlich Adsorption Isotherm F-

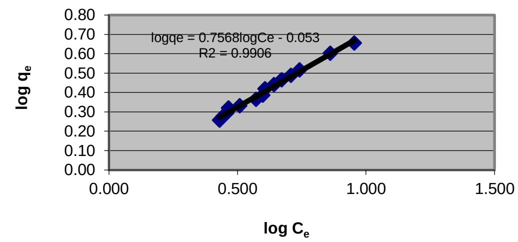

Fig. No. c

Linearised Langmuir Adsorption Isotherm F-400-Raw Carbon -Ni^{2+}

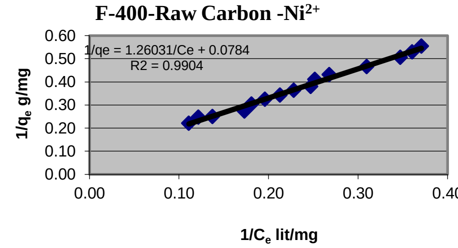

Fig. 1. Single Solute Adsorption And Simultaneous Recovery

As 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. In modification 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 some time. 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.

Single solute adsorption system it was observed that the different metal ions were adsorbed up to different extent by the raw GAC. Digesting the adsorbed GAC in concentrated HNO_3 carried out the recovery of nickel. In this process raw GAC adsorbed with nickel ions was digested with a small amount of concentrated HNO_3 and then the solution diluted to a fixed volume and analyzed for nickel ion. In this process the copper ions are converted to their corresponding nitrates. The nickel balance checked by this process was found to be very satisfactory.

F-400 GAC

Wt. of F-400 GAC = 0.5 gm

Volume of solution = 200ml

Table III. Recovery of Nickel by RGACF-400

Sr. No	Initial amount of Nickel in solution in mg/ml	Amount of Nickel Recovered mg
1	5.316	5.251
2	5.316	5.201
3	5.316	5.240

CONCLUSION

The following are of the important aspects of the present investigation.

1) When the metal ions adsorbed granular activated carbons were digested with concentrated HNO_3, the metal
recovery was very much conclusive.

2) The carbon treated with suitable oxidizing agent played a significant role in the recovery of metal ions.

3) Nickel on the GAC, the surface is saturated with a monolayer of Nickel ion is observed with a satisfactory
results.

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