
ORIGINAL ARTICLE

Adsorption and Kinetics Study of RGAC and MGAC as an Adsorbent to Remove Heavy Metal Ions from aqueous solution By Surface Technology

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ABSTRACT

Adsorption on activated carbon is a promising technique for the treatment of low-concentration heavy metal pollutants in water with high efficiency and simple operation. Activated carbon is the most popular adsorbent and produces the best results, but its use is constrained by its expensive price. Its production and regeneration costs are significant. Freshwater resources are in low supply in the world today, thus finding alternatives that reduce the strain on the available resources is inevitable. Additionally, heavy metals are poisonous even at trace amounts, therefore inexpensive adsorbents were necessary for a method of heavy metal removal that was safe for the environment. Adsorption is a cost-effective method that has gained popularity for its minimal waste disposal benefit. Therefore, much attention has been given to cost effective Granular Activated Carbon(GAC). In this work, adsorption of Ni^{+2}, Co^{+2} ions in aqueous solutions was conducted using granular-activated carbon, after surface modification Modified Granular Activated Carbon(MGAC) using different methods. The adsorbents were obtained in granular form which facilitates all steps of the use, recovery, and reuse of the material, differently from the powdered-activated carbon normally used. The estimated amount of the solute that is adsorbed on the surface of the adsorbent per unit weight as a function of equilibrium concentration at a fixed temperature is represented by adsorption isotherms. The two isotherms that are most frequently used to explain the adsorption process in this article are the Langmuir and Freundlich isotherms.

KEYWORDS: Granular Activated Carbon, Modified Granular Activated Carbon, Heavy Metal Ions, Adsorption.

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INTRODUCTION

Heavy metals, such as Zn, Fe, Cu, Cr, Hg, Pb, Ni, Co, and others, are hazardous elements with specific gravities larger than 5g/cm³. Heavy metals are primarily produced by volcanic activity, rock weathering, and soil erosion. The anthropogenic sources, however, include industrial processes including mining, metal processing, chemical fertiliser production, dye making, and fuel burning. Due to their non-biodegradability, recalcitrance, and high mobility in aqueous media, heavy metals tend to accumulate in soils and living things, which has an adverse effect on the ecosystem. Because they are carcinogenic, heavy metals are absorbed by plants and biomagnify through food chains in animals and people, having substantial adverse health effects [2, 3, 4, 5]. Heavy metals can cause serious harm to the environment and human health because most of them are toxic, mutagenic and carcinogenic [6] The entry of heavy metals into human living environments they are penetrating into our body by water, air, food or absorption through skin. Air (industrial and burnt fuel), soil (fertilizer, pesticides, insecticides, etc.) and water (industrial wastewater, rock, etc.) are main sources of heavy metal by which they are accessible in environment. [7,8]. Heavy metal may be affect on nervous system, damage various body organs such as liver, kidney, lungs, brain, and blood, causes Alzheimer disease, etc.[9] Toxic effects of various metals were reviewed by various scientists[10-12]. Great efforts have been made to develop efficient techniques for heavy metal removal in recent years, such as ion exchange [13] chemical precipitation,[8]

electrochemistry,[9] membrane filtration,[14] and adsorption.[15] The carbon-based adsorption technique is widely applied in environmental protection, and biomass-derived activated carbon is recognized as one of the most economical and promising adsorbents for heavy metal removal. Activated charcoal is used as an adsorbent due to its remarkably high porosity, enhanced pore size and higher adsorption capacities.

It is recognized as one of the most economical and promising adsorbents for heavy metal removal. Fig 1 shows recent publications obtained searching for "Heavy metal pollution" and "Removal of heavy metal" in Topic via Web of Science. As can be seen, there were over 3500 publications related to heavy metal pollution and over 2500 publications associated with the removal of heavy metals in the period of 2018–2022.

The carbon-based adsorption technique is widely applied in environmental protection, and Granular activated carbon and Modified activated carbon. In this paper, the feasibility for adsorption of heavy metals onto AC-NLP was analyzed using batch study. Several process parameters like temperature, adsorbent dose and contact duration; thermodynamic studies and chemical kinetic analyses were conducted for batch treatment. Different isotherms were utilized for evaluation the performance by their capacities. Also, experiments of regeneration of GAC were conducted.

MATERIAL AND METHODS

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

Balance :The balance used for weighing was a electronic balance with an accuracy of +

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

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 $28^{\circ} \pm 0.1^{\circ}\text{C}$.

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-100, F-200, F-300 and 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

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

Preparation of the Solution of metal ions and their estimations.

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 [19].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 [20]. 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 Tables.

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 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**

ADSORPTION ISOTHERM OF NICKEL METAL ION ON RAW GAC AND MODIFIED GAC.

The adsorption isotherms of metal ions like Ni, Co on various grades of raw GAC and oxidized GAC i.e. F-400, F-300 as mentioned in previous chapter. 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.

$$q_e = (C_0 - C_e) \times V/W$$

Where

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

C_0 = 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 [18]

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

Where Q° = amount adsorbed per unit weight of the adsorbent forming a complex 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

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

Permitting calculation of Q° . The value of Q° 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° 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.

The equation is $q_e = KC_e^{\beta}$

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

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

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

RESULT AND DISCUSSION

Table -1 Adsorption Isotherm F-400 - Raw Carbon-Ni²⁺

Sr. No.	Metal ion	Grades of raw GAC	Q° g/mg	$A \cdot 10^{-16} cm^2$	$S \text{ cm}^2/gm$	$S' \text{ cm}^2/gm$
1	Ni ²⁺	F-300	71.4285	5.244	2.256×10^{10}	2.13×10^{10}
2	Ni ²⁺	F-400	83.3333	5.244	2.632×10^{10}	2.43×10^{10}

Figure 1: Adsorption Isotherm F-400 - Raw Carbon-Ni²⁺

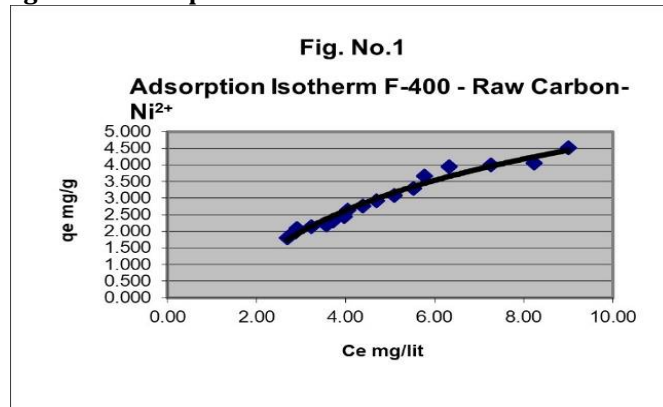


Figure 2: Linearised Freundlich Adsorption Isotherm F-400-Raw Carbon -Ni²⁺

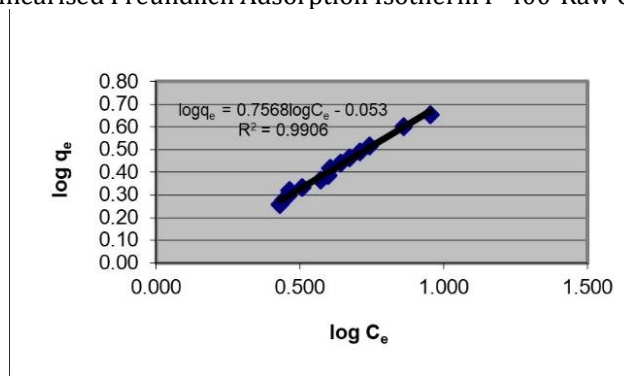


Figure 3: Linearised Langmuir Adsorption Isotherm F-400-Raw Carbon -Ni²⁺

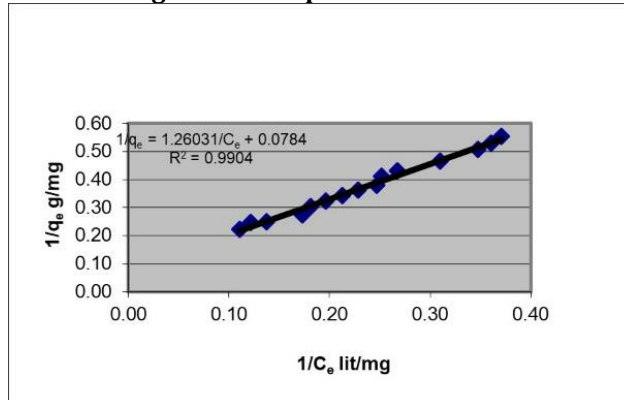
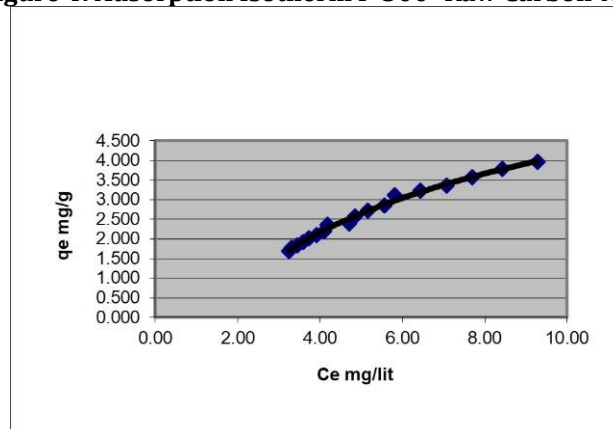


Figure 4: Adsorption Isotherm F-300 -Raw Carbon-Ni²⁺



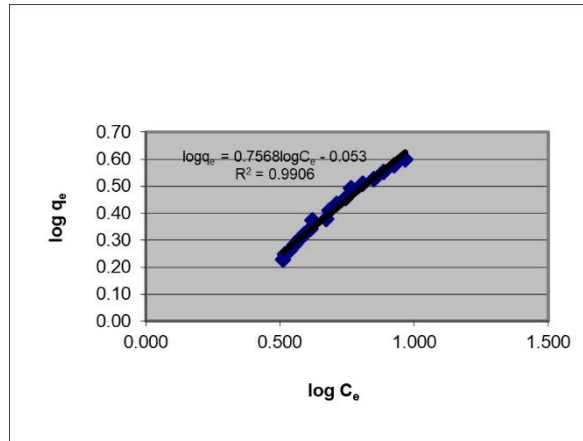


Figure 5: Linearised Freundlich Adsorption Isotherm F-300-Raw Carbon -Ni2+

Figure 6: Linearised Langmuir Adsorption Isotherm F-300-Raw Carbon -Ni2+

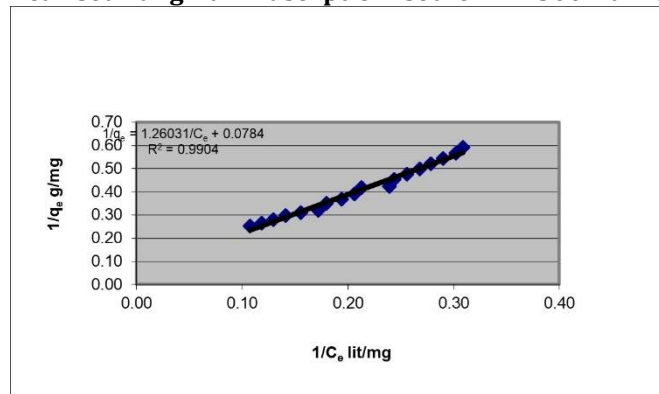


Table-2

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	Ni ²⁺	F-300	142.857	5.244	4.512 x 10 ¹⁰	4.037 x 10 ¹⁰
2	Ni ²⁺	F-400	166.667	5.244	5.264 x 10 ¹⁰	4.766 x 10 ¹⁰

Figure 7: Adsorption Isotherm F-400 - Oxidised Carbon-Ni2+

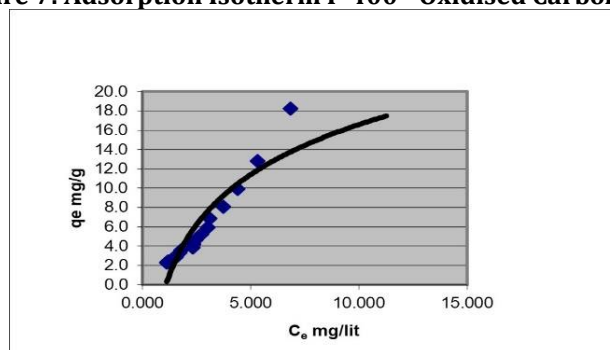


Figure 8: Linearised Freundlich Adsorption Isotherm F-400-Oxidised Carbon -Ni²⁺

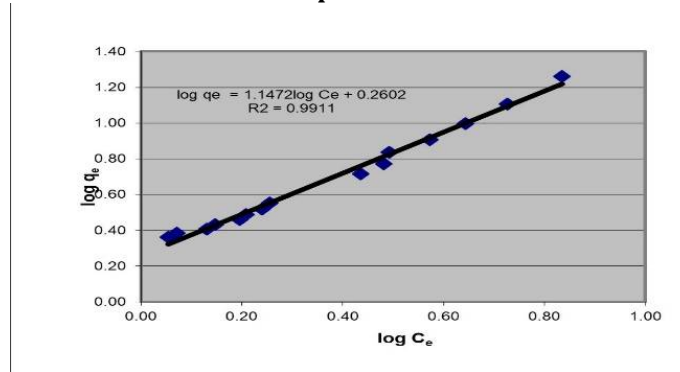
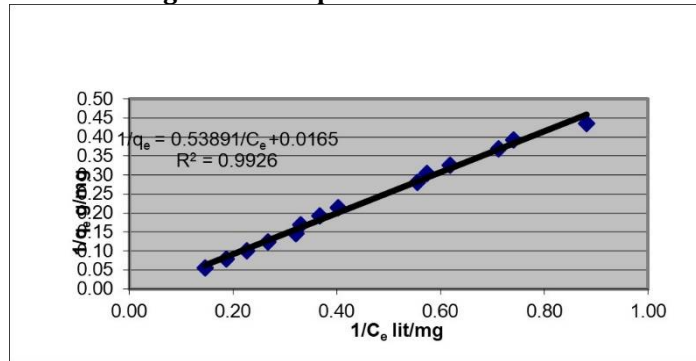


Figure 9: Linearised Langmuir Adsorption Isotherm F-400-Oxidised Carbon -Ni²⁺



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

$$F-400 > F-300$$

However utilizing could roughly assess the values of the area occupied by metal ions on the modified GAC when the surface is saturated with a monolayer of metal ion could be roughly assessed by utilizing the values of q_{emax} in mg per gm of carbon and converting it to atoms per gm of carbon by the relation.

SINGLE SOLUTE ADSORPTION AND SIMULTANEOUS RECOVERY.

From the batch experiments of the 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 HNO₃ carried out the recovery of Nickel . In this process raw GAC adsorbed with copper ions was digested with a small amount of concentrated HNO₃ and then the solution diluted to a fixed volume and analyzed for Nickel ion. In this process the Nickel ions are converted to their corresponding nitrates. The Nickel balance checked by this process was found to be very satisfactory. The results are given in Tables

Table 3: Adsorption of Nickel on raw F-400 GAC
Wt. of F-400 GAC = 0.5 gm
Volume of solution = 200ml

Sr No	Initial amount of Nickel in solution in mg/ml	Final amount of Nickel in solution in mg/ml	Amount of Nickel adsorbed by GAC in mg/gm
1	791.2	459.2	332.0
2	791.2	458.0	333.2
3	791.2	455.2	336.0

**Table 4: Recovery of Nickel by digesting the adsorbed F-400 GAC
With concentrated HNO₃
Wt. of F-400 GAC =0.5 gm
Volume of solution = 200ml**

Sr No	Nickel recovered in mg/gm	Nickel present in reference carbon in mg/gm	Resultant Nickel recovered in mg/ml
1	332.0	29.8	302.2
2	333.2	24.1	309.1
3	336.0	24.4	311.6

The recovery of nickel and cobalt ions is in good agreement with the amount of same metal ions adsorbed. It is therefore evident that other metal ions could be scavenged and recovered this way.

Environmental Significance

The most important environmental issue that each nation is currently dealing with is the removal of heavy metal ions from aquatic solutions. According to current literature reviews, the most prevalent pollutants in groundwater were found to be heavy metals. The removal of suspended or dissolved heavy metal from wastewater necessitates the use of low-cost materials and a variety of conventional processing techniques, including adsorption, electrodeposition process, distillation or evaporation, filtration, flotation, ion exchange, precipitation, ultra-filtration, neutralization, precipitation, sedimentation, reverse osmosis, and solvent extraction. Since activated carbon has a high resultant active surface area, big mesopore and Micropore volumes, and is an excellent adsorbent, it is widely utilized to remove heavy metal contaminants.

CONCLUSION

It is observed that, When the metal ions adsorbed granular activated carbons were digested with concentrated HNO₃, the metal recovery was very much conclusive. The carbon treated with suitable oxidizing agent played a significant role in the recovery of metal ions. Technique was found to be useful in the separation of particular metal ion from the mixture of metal ions. Modifying the carbon surface with oxidation by Nitric acid in order to obtain maximum recovery of a given metal ion optimized the recovery process. The oxidizing agent such as Nitric acid played an important role in the modification of the carbon surface was found to be better using oxidizing agents compared to use of raw carbon.

In summary There are other kinds of isothermal adsorption relations that can happen, but the most prevalent one is when the adsorption results in the apparent deposition of a single layer of adsorbate molecules on the adsorbent's surface. The Langmuir adsorption, but more intricate adsorption models need to be taken into consideration for multimolecular adsorption.

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