



Study on Adsorption and desorption Characteristics of Heavy Metal Ions from Aqueous Solutions by GAC Adsorbent.

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ABSTRACT:

Over the past few decades, adsorbents have significantly increased in efficiency and economy when it comes to removing heavy metals and metalloids from water. However, the recovery of heavy metals from the desorbing agents and the recycling of spent adsorbents received less attention. Numerous researchers tried a variety of potential regenerating agents, such as acids, alkalis, and chelating agents, for the regeneration and reuse of adsorbents, with varying degrees of success in some experiments confined to a small number of adsorption–desorption cycles. The recovery of adsorbed (from GAC adsorbents) and desorbed (from regenerating agents) metals was the main focus of only a small number of the published research.

While managing used adsorbents and recovering heavy metal ions is crucial, the fate of wasted adsorbents prior to disposal has not been extensively studied in research studies. The removal and desorption efficiencies of various adsorbents and regenerating agents, as well as the heavy metal recovery from saturated adsorbents and desorbing solvents utilized in regeneration, are summarized in this paper. The results of this study will assist the scientific community conducting adsorption studies in pursuing the necessary research projects to address practical heavy metal recovery techniques from utilized adsorbents, investigate potential repurposing of desorbing agents, and select an appropriate desorbing/regenerating agent for a given adsorbent.

Introduction:

Water is essential for life, but its quality has been increasingly compromised by modern industrial activities [1, 2]. Ensuring the provision of safe and high-quality water is a paramount global concern [3, 4]. The contamination of clean water supplies by heavy metals and dyes poses significant threats to human health, animal well-being, and ecosystem integrity. Heavy metals, including cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), arsenic (As), and mercury (Hg), are among the most concerning pollutants due to their acute toxicity and adverse effects on human health and aquatic ecosystems [5, 6]. Chronic exposure to heavy metals can lead to severe toxicological consequences, including neurological damage and skin irritation, with chromium (Cr) and

arsenic (As) being particularly harmful. Various wastewater treatment approaches have been developed to address heavy metal contamination [7]. These include physical, chemical, and biological methods such as adsorption, membrane filtration, ion exchange, reverse osmosis, membrane bioreactors (MBRs), and microbial remediation. However, challenges related to cost-effectiveness, efficiency, and sustainability hinder the widespread applicability of these techniques [8,9]. The presence of these metals in the environment is now a grave matter of concern. To minimize the health risk and for the management of environmental degradation, strict quality standards were imposed for both drinking water and effluent discharge. Compliance with these strict standards is now a major challenge for the industries, drinking water providers and scientists



alike for proper treatment of groundwater, surface water and industrial wastewater containing heavy metals[10] There are several physical, chemical or biological techniques that are used for the treatment of groundwater, surface water and wastewater such as coagulation, filtration, flocculation, adsorption, reverse osmosis, activated sludge process, chemical precipitation, membrane separation process and bioremediation. Conventional methods for treating effluents, such as precipitation, redox, membrane technologies and electrolysis, are costly and have problem of secondary waste generation (sludge)[11]The safe disposal of sludge is another issue for the industries [12]. Heavy metal(s) and metalloid (arsenic) removal techniques include coagulation and flocculation, precipitation, adsorption, ion exchange and membrane filtration. Alternative methods such as ozone oxidation, bioremediation and electrochemical treatments are also used in the removal of arsenic[13-16].Among the various available techniques for water and wastewater treatment for heavy metal removal, adsorption is considered as the most attractive technique[17]. Adsorption technique has several advantages over other techniques, such as it is easy to implement in field condition, it has the potential regeneration capacity and the operation is sludge free, and has a high removal efficiency of metal ions.[18-20]. Continuous improvements are being reported for the development of effective and suitable adsorbents for achieving higher removal efficiency[21] found different types of adsorbents such as (1) activated carbon, (2) carbon nanotubes,(3) low-cost adsorbents and (4)Various studies were reported for removal of heavy metals using various adsorbents to achieve a desirable target of removal efficiency. Adsorption on activated carbon has been found to be superior compared to other chemical and physical methods for both water and wastewater treatment in terms of its capability for efficiently adsorbing a broad range of pollutants, fast adsorption kinetics and its simplicity in design.[22-23].Adsorption and desorption are the primary mechanisms driving the interactions of heavy metals with water and sediments[24].The toxicity risks posed by heavy metals to aquatic environments and, eventually, to human health, are closely related to their partitioning between the particulate and aqueous phases .Unlike organic pollutants, heavy metals are non-biodegradable and

persist in the environment redistributing among the environmental compartments, including sediments, water and living organisms [25] Moreover, less attention has been paid to the disposal or recycling of used adsorbents containing adsorbed heavy metals.[26] The efficiency of bio-adsorbents for removal of heavy metal(s) and suggested that biosorption depends on the efficiency of the regeneration of bio-adsorbents after metal desorption. The disposal of used adsorbents containing heavy metal(s) may be done after recovery of contaminants or directly without heavy metal recovery, but in both the cases there will be secondary pollution from the used adsorbents and the chemicals used to treat the adsorbents for metal recovery [26].However, metal-loaded adsorbents have toxic effects on humans and environment. Therefore, the used adsorbents should be released into the environment only after recovery of the heavy metals completely. Considering the need of metal desorption and recovery, this paper summarizes the efficiency of various regenerating agents used by different authors, efficiency of the adsorbents for removal of heavy metals, and recovery of heavy metals.

Methods and Materials :

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.

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.

Experimental Outline of present work:

- Choice of adsorbent from various grades of the adsorbents available in the laboratory.
- Processing and characterization of the adsorbent used in the present work.
- Choice of metals and preparation of their solutions and estimation of solutions of Co^{2+} , $\text{Cr}_2\text{O}_7^{2-}$, Cu^{2+} , Ni^{2+} .
- Preparation of the solution of the co-metal ions and their separations using Granular Activated Carbon and Oxidized Granular Activated Carbon.
- Experimental arrangement and method for carrying out adsorption equilibrium studies.

Result and Discussion:

Determination of adsorption isotherm of Cobalt on Raw Granular Activated Carbon(F-400) and Modified Granular Activated Carbon(F-400).

For determining the adsorption isotherm of Cobalt 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, and fixed concentration of 200ml of Cobalt ion in solution was then introduced. The stirrer was placed in position and the contents were stirred for six hours at 28°C . The initial and final concentration of Cobalt 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 Cobalt adsorbed on the GAC was determined by following expression.

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

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

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

C_e = Equilibrium concentration of Cobalt ions in solution in mg per lit.

V = Volume of solution taken in liters.

W = Weight of carbon taken in grams.

Thus for each GAC- Cobalt on 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 Cobalt 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 are given in **Fig.**

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. 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 2.

Experimental arrangement and method for carrying out adsorption studies

To determine the adsorption isotherm of co-metal ions (Cr, Ni, Co, Cu) 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. The contents were stirred using a paddle type glass stirrer with the help of Remi stirrers (Model RQ 122) whose speed could be regulate by any desired value. 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 $\pm 0.5^\circ\text{C}$.

At first, a one liter of round bottom flask was introduced into the tub bath and different weights of GAC or OGAC (Oxidized Granular Activated Carbon) 0.1 gm to 1 gm carbon each time was stirred with 200 ml each of same concentrations of metal ions in this flask using the glass paddle stirrer fitted to the Remi motor. 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 sped 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.

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

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 lit.

V = Volume of solution taken in liters.

W = Weight of carbon taken in grams.

Table 1

Adsorption Isotherm data of Cobalt on raw and modified F-400 GAC

Wt. of F-400 GAC = 0.5 gm

Volume of solution = 200ml

| Sr . No. | Metal ion | Grade s of modified GAC | Q^0 g/mg | A 10^{-16}cm^2 | S cm^2/g m | S' cm^2/g m |
|----------|-----------|-------------------------|------------|--------------------------|----------------------------|-----------------------------|
| | | | | | | |



| | | | | | | |
|---|------------------|-------|-------------|-----------|-----------------------------|-----------------------------|
| 1 | Co ²⁺ | F-400 | 33.33 33 | 5.32 2 | 1.068 x 10 ¹⁰ | 1.165 x 10 ¹⁰ |
| 2 | Co ²⁺ | F-400 | 71.42 85 | 5.32 2 | 2.228 x 10 ¹⁰ | 2.44 x 10 ¹⁰ |

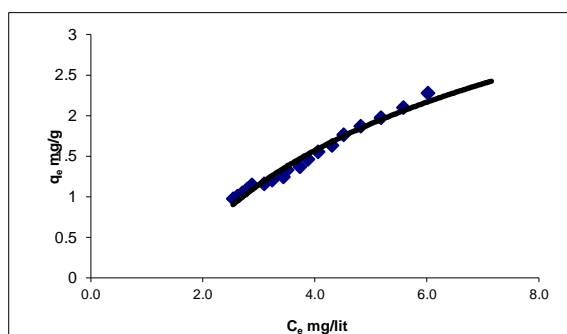
TABLE 2

Adsorption of Cobalt on raw F-400 GAC

Wt. of F-400 GAC = 0.5 gm

Volume of solution = 200ml

| Sr No | Initial amount of Cobalt in solution in mg | Final amount of Cobalt in solution in mg | Amount of Cobalt adsorbed by GAC in mg/ml |
|-------|--|--|---|
| 1 | 110.1 | 100.1 | 9.90 |

Fig. No.1: Adsorption Isotherm System: F-400-RawGAC -Co²⁺

| | | | |
|---|-------|-------|-------|
| 2 | 110.1 | 100.2 | 10.00 |
| 3 | 110.1 | 100.1 | 9.90 |

TABLE 3

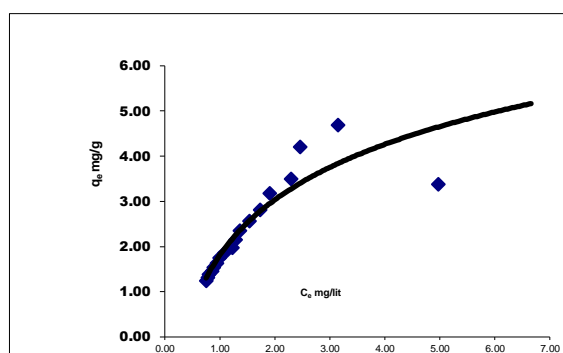
Recovery of Cobalt by digesting the adsorbed F-400 GAC

With concentrated HNO₃

Wt. of F-400 GAC =0.5 gm

Volume of solution = 200ml

| Sr No | Cobalt recovered in mg/ml | Cobalt present in reference carbon in mg/gm | Resultant Cobalt recovered in mg/ml |
|-------|---------------------------|---|-------------------------------------|
| 1 | 9.90 | 6.75 | 3.15 |
| 2 | 10.00 | 7.00 | 3.00 |
| 3 | 9.90 | 6.95 | 2.95 |

Fig. No.2: Adsorption Isotherm System:F-400-Oxidised GAC - for Co²⁺**Conclusion:**

The current project was started with the knowledge that hazardous metals in wastewater could have a major negative impact on living things. According to current literature reviews, adsorption with granular activated carbon is a very practical and affordable method for removing these hazardous elements from wastewater. Basic chemistry related to the diffusion of metal ions in the macro and micropores of carbon is involved in the adsorption of metal ions on both raw activated granular

carbon and oxidised carbon. Among the significant facets of the current study are the following.

- 1)The metal recovery was overwhelmingly conclusive when the concentrated HNO₃ was used to decompose the granular activated carbons that had been adsorbed with metal ions.
- 2) The recovery of metal ions was significantly aided by the carbon that was treated with an appropriate



oxidizing agent.

3) The technique proved effective in separating a specific metal ion from the metal ion mixture.

4) Optimising the recovery process by modifying the carbon surface by nitric acid oxidation to

achieve maximal recovery of a specific metal ion.

5) It was discovered that employing oxidising chemicals, such as nitric acid, was preferable to using raw carbon in the modification of the carbon surface.

7) Attempts have been made to regenerate and reuse the spent carbon which could undoubtedly help in

making chemistry as green as possible when the carbon is regenerated, its adsorption capacity increases considerably.

8) From kinetic studies, it was observed that for the first 60 minutes adsorption rate is high and thereafter it practically remains constant. This is probably due to surface diffusion of metal ions in micro and macropores of carbon.

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