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ADSORPTION MECHANISM OF HEAVY METAL IONS ON GRANULAR ACTIVATED CARBON.

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Abstract :
Granular Activated carbon was used as environment friendly adsorbents in the present study. This study focuses on the investigation of the adsorption ability of various heavy metal ions from aqueous solution. The adsorption of heavy metals onto GAC and MGAC was dependent on particle size, dose, solution pH, contact time, and temperature. Kinetic data were tested using various kinetic models. Langmuir and Freundlich models have been applied to calculate adsorption data . The results suggests that the adsorption of heavy metals by the GAC was a spontaneous process. Thus, it was concluded that GAC and MGAC are promising adsorbents for the adsorption of heavy metals from aqueous solutions

Key words: Heavy Metal Ions ,Granular Activated Carbon, Adsorption.

Introduction:-

Heavy metal pollution sources include environmental, hobbies, industrial, water supply, and others. Zn, Cu, Pb, Cd, Cr, Hg, and As are the most common toxic heavy metals in water system; therefore, the pretreatment of wastewater containing heavy metal will be required [1]. To improve water quality for effluents from industrial facilities and wastewater treatment, increasing awareness for development of systems has provided incentives to improve performance of existing technologies, or develop new technologies. Various methods exist for the removal of metal ions from aqueous solutions, but adsorption is by far the widely used and most versatile process [2].The current proliferation of technology and development of science have been an enormous boon for humans. They have become dependent on technology and scientific development in various aspects such as daily activities, trade, industry, and work.Heavy metals are structural elements such as lead, zinc, arsenic, cadmium, copper, titanium, cobalt, lithium, aluminum and mercury,and can be in the form of metals or dissolved salts.These metals are present in the environment in air, water, and soil. For example, factory chimneys release metal oxides into the air, thus transmitting heavy metal pollution to humans, animals and plants. In addition, car exhausts release lead oxides, resulting from the combustion of tetraethyl lead, into the atmosphere and this is one of the most widespread routes to leading contamination of marine organisms with metals, and the transit these contaminants via sea fishing to humans and animals. Furthermore, agricultural soil is one of the most important sources of food polluted by The aim of this work is to study the adsorption of heavy metals from water using nanoparticle of abundant wild herbs, which are considered environmentally safe and low-cost. The particle size,dose, solution pH, contact time, and temperature were investigated.Thermodynamic parameters, kinetic, equilibrium and adsorption isotherms were determined to analysis of the adsorption behavior heavy metals, which arises through the irrigation of crops with polluted water or the use of pesticides. In this situation, the metals are transmitted through the vascular system of plants and fruits.Therefore, field crops irrigated with drainage water contaminated by heavy metal ions are one of the most important and most dangerous sources for the entry of poisonous heavy metals into the human body[3].

There are many methods adsorption of heavy metals from the environment, both chemical and physical. However, some of these are not economically feasible. Therefore, it is necessary to investigate low-cost effective alternatives. The adsorption of heavy metals by adsorption technology is a good alternative, and it is used in the treatment of wastewater and soil. To compare, the adsorbent substances, the cost, as well as effectiveness, must be considered.Activated carbon is a highly effective adsorption substance of heavy metals from wastewater, but it is soluble under extremelyacidic conditions[4].

Consequently, there is an increased interest from researchers into low-cost, effective alternatives adsorbents. Many natural materials used in the adsorption of heavy metals (cadmium, copper, chromium, lead, nickel, cobalt, and lithium), have been discovered,such as diplotaxis harra, glebionis coronaria, coffee

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grounds,banana Peel, fruit and vegetable peels, cactus, rice straw, wheat straw, and salvinia plant[5,6,7,8,9].

The aim of this work is to study the adsorption of heavy metals from water using nanoparticle of abundant wild herbs, which are considered environmentally safe and low-cost. The particle size,dose, solution pH, contact time, and temperature were investigated. Thermodynamic parameters, kinetic, equilibrium and adsorption isotherms were determined to analysis of the adsorption behavior.

The present work required some prerequisites in the laboratory to enable smooth experimentation.

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

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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.

10) **Preparation of the solution of co-metal ions and their separations using Oxidized Granular Activated Carbon**.

In the present work while studying the scavenging of co-metal from the solution, it was necessary to prepare these solutions and estimate them so that their concentrations in solution during experimentation could ascertain. To separate one metal from another one in the solution using oxidized granular activated carbon, which is modified with oxidizing agents, carried out experiments. In the present work experiments were carried out to start with the following metals ion mixtures to study their removal leading to separation techniques.

a. Mixture of Chromium and Cobalt in solution

The above metals are found in industrial wastes, found in the combined state in earth's crust and also found together in some of the important alloys hence these metals were chosen for the experimental work.

11) Mixture of Chromium and Nickel in solution.

A solution mixture of Chromium and Nickel was prepared by taking four different concentration (ratio) i.e. 10:10, 10:16 and 10:20 of Cr:Co metal ions respectively. Fixed amount of standard stock solution of Chromium mixed with fixed amount of standard stock solution of nickel and the entire solution was diluted. Thus different concentrations of nickels ions were obtained keeping the concentration chromium metal ion fixed. The weight of oxidized carbon was taken from 0.1gm to 1gm for about 6 hours. The carbon was then filtered off and was washed properly with distilled water. Finally the filtered was checked for the residual concentration of both chromium and nickel ions by usual colorimetric analysis outlined earlier. The results are given in

Table

Modification of carbon surface with oxidizing agent

Carbon surface was modified by two ways The granular activated carbon adsorbed with metal ion was first incinerated in a muffle furnace at 800°C ± 15°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.

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Granular activated carbon modified by concentrated nitric acid and this process is called as chemical modification of the carbon surface, which involved following procedure. 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.

Determination of adsorption isotherm of mixture of Chromium and Cobalt on different grades of granular activated carbon.

For determining the adsorption isotherm of mixture of Cobalt and Chronium 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 nickel 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 and Chronium 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.

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

Where

q_e = Concentration of Cobalt and Chronium ion on GAC in mg/gm of carbon
C_o = Initial concentration of Cobalt and Chronium ions in solution in mg/liter.
C_e = Equilibrium concentration of Cobalt and Chronium ions in solution in mg Per liter.
V = Volume of solution taken in liters.
W = Weight of carbon taken in grams.

Thus for each GAC- Cobalt and Chromium ion 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 nickel ion on different grades of GAC. The data on these isotherm are given in **Table** , 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 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.**

Adsorption Isotherm Of Co-Metal Ion On F-400 Modified Gac.

Similar set of experiments were carried out as mentioned above in adsorption isotherm of co-metal ion on modified F-400 oxidized carbon. Only difference is that in this adsorption study the mixture of solution of different metal ions were carried out on modified F-400 carbon, where the modification of carbon was discussed earlier.

Similar procedure was followed for the mixture of Cr: Co and Cr: Cu at four different concentrations discussed as follows.

Above similar procedure was applied for Oxidized granular activated carbon for F-400 and also for the mixture of Cobalt and Chromium for determining adsorption isotherms.

In the mixture solution four different concentration (ratio) of metal solution takes place like 10:10, 10:16, 10:20 for Cr: Co respectively, in this concentration the concentration of Cr kept constant and Co was varied. In second system at the same ratio of the concentration chromium was varied and nickel kept constant.

Result and Discussion :

Sr No	Metal ions	Concentration of Metal ions	Grades of Modified GAC	q_{emax} for Cobalt in mg/gm

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1	Cr:Co	10:10	F-400	0.303
2	Cr:Co	10:16	F-400	0.392
3	Cr:Co	10:20	F-400	0.401
4	Co:Cr	10:16	F-400	0.275
5	Co:Cr	10:20	F-400	0.265

r. No.	Metal ion	Grades of modified GAC	Concentration of Metal ions	Q^o g/mg for Cobalt	A $10^{-6}cm^2$	S cm^2/gm for Co	S′ cm^2/gm for Co
1	Co:Cr	F-400	10:10	4.7619	5.322	1.526×10^{10}	1.649×10^{10}
2	Co:Cr	F-400	10:16	4.0000	5.322	1.282×10^{10}	1.497×10^{10}
3	Co:Cr	F-400	10:20	4.7619	5.322	1.526×10^{10}	1.442×10^{10}
4	Cr:Co	F-400	10:16	6.6666	5.322	2.136×10^{10}	2.133×10^{10}
5	Cr:Co	F-400	10:20	7.1428	5.322	2.289×10^{10}	2.182×10^{10}

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 Ce the Langmuir equation could be expressed as follows

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

Where Q^o = 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 mg/gm.

b = Langmuir constant

Rearranging the above expression

$$1/q_e = l/(Q^o.b.C_e) + 1/Q^o$$

A plot of $1/q_e$ versus $1/C_e$ should be linear if Langmuir adsorption were Permitting calculation of Q^o. The value of Q^o 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:

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

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^o 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 $q_e = KC_e^{\,B}$

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.

$$\text{Log } q_e = \log k + \beta \log C_e$$

Similarly discussed as above the mixture of Cr and Co kept by varying the concentration of Co and fixed concentration of Cr as 10:10, 10:13, 10:16,10:20 for Cr:Co respectively. From the results it was observed that the presence of chromium hinders the adsorption of copper. The surface area and the q_{emax} was reported in Table.

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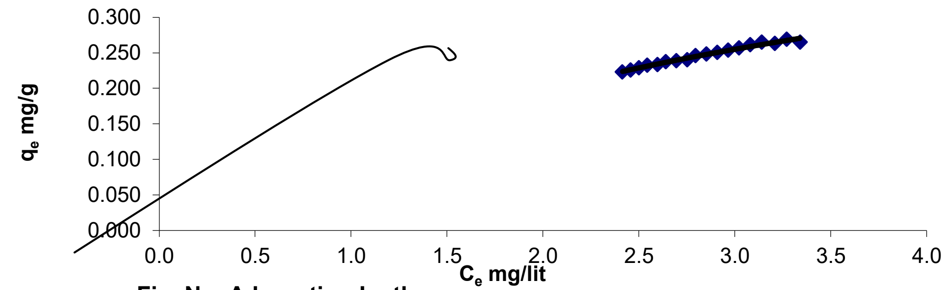

Fig. No. Adsorption Isotherm
System: F-400 -Oxidised GAC-CO^{2+}in presence of - Cr^{6+}

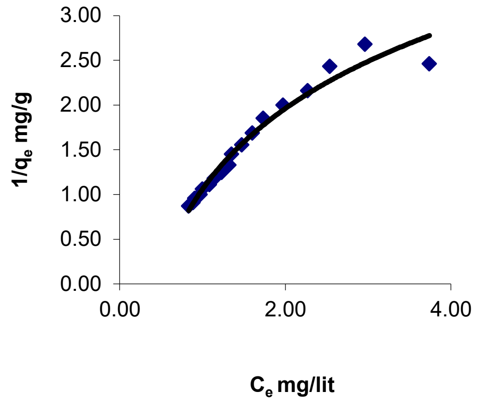

Fig. No. Adsorption Isotherm
System: F-400-Oxidised GAC - $Cr_2O_7^{2-}$in Presence of- Co^{2+}

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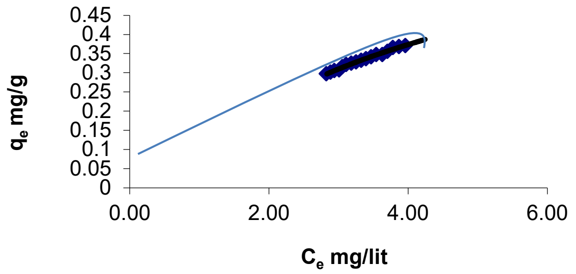

Fig. No. :Adsorption Isotherm F-400 - Oxidised Carbon-Co^{2+}in presence of -

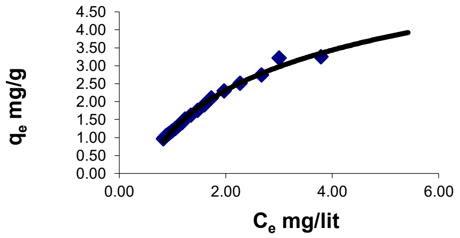

Fig. No : Adsorption Isotherm System: F-400-Oxidised GAC -$Cr_2O_7^{2-}$ in presence of- Co^{2+}

By taking the proportion of Co:Cr as 10:10, 10:13, 10:16,10:20 respectively, it was observed that, the presence of cobalt hinders the adsorption of chromium. The surface area and the q_{emax} value was reported in Table

Conclusion

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.

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