HEAVY METALS REMOVAL FROM MEDICINAL PLANTS USING GRANULAR ACTIVATED CARBON AS ADSORBENT BY SPECTRAL METHOD

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ABSTRACT

Medicinal herbs are easily contaminated by metals of concern are arsenic (As), cadmium (Cd), copper (Cu), Mercury (Hg) and lead (Pb) due to factors such as environment, pollution, atmosphere, soil, harvesting and handling. Heavy metals confined in plants finally enter the human body and may disturb the normal functions of central nervous system, liver, lungs, heart, kidney and brain, leading to hypertension, abdominal pain, skin eruptions, intestinal ulcer and different types of cancers. Removal of the heavy metal ions from contaminated medicinal plants such as Glycyrrhiza glabra (Root), Plumbago zeylancia (Root), Salacia Oblonga (Root) and Lannea coromandelica (Bark) by adsorption technique. It, therefore, becomes necessary to remove these heavy metals from medicinal plants by an appropriate treatment before consuming. Adsorption technique is the best, economically viable and efficient method for the treatment of heavy metal ion contaminated in medicinal plants. Removal of the heavy metal ions from aquatic environment by the adsorption on the Granular activated carbon applying batch technique attracts special attention due to its well-known low expensive nature and high efficiency.

Key words: Adsorption technique, Granulated activated carbon, , Heavy metals and Atomic absorption spectrometry.

1.0 Introduction

The purpose of this study was to investigate the removal of some toxic heavy metals from Medicinal Plants by adsorption, to determine the optimum removal condition. Heavy metals contamination in medicinal plants can originate from atmospheric pollution, pesticides and chemical fertilizers etc., Heavy metals like As, Cd, Cu, Hg, Pb etc., are toxic metals cause health problems while consuming the medicinal plants contaminated with heavy metals.

So in order to ensure that the contribution from the plants is not high, there was need for the analysis of the plants before it is being used for preparation of medicine. Hence a set of commonly used medicinal plants were taken for a preliminary study of their toxic elemental content using the technique of AAS.

1.1 Permissible limits

The Government of India, Department of AYUSH, Ministry of Health and Family Welfare has issued new safety standards for the ayurvedic drugs. The permissible limits of the heavy metals in ayurvedic drugs with herbal ingredients as per WHO (World Health Organisation) and Department of AYUSH are Arsenic (As)- 3 ppm, Cadmium (Cd)- 0.3 ppm, Copper (Cu)- 30 ppm, Lead (Pb)- 10 ppm, Mercury (Hg)- 1 ppm. In the present study, the heavy metals such as arsenic, cadmium, lead, mercury and copper were determined in medicinal plant samples collected from different sources.

2.0 Removal of heavy metals using activated carbon as Adsorbents

Removal of these toxic metal ions are the best approaches to control the metal pollution problem and safeguard the environment and human health.Activated carbon is widely used as an adsorbent in industry due to its high adsorption capacity. This capacity is related to the pore structure and chemical nature of the carbon surface in connection with preparation conditions.

2.1 Adsorption studies of heavy metals

The present investigation deals with the studies of simultaneous removal of heavy metal ions such as As^{3+}, Cd^{2+}, Co^{2+}, Hg^{2+} and Pb^{2+} by adsorption on the commercially available adsorbent Granulated Activated Carbon (GAC). Results of various parameters like Initial concentration of metal ions in medicinal plants, Contact time and pH of the solution affecting the adsorption process, kinetic of adsorption are presented and discussed.

2.2 Effect of Initial Concentration of the metal ions

Adsorption studies of heavy metal ions As^{3+}, Cd^{2+}, Co^{2+}, Hg^{2+} and Pb^{2+} on GAC at a fixed dose of adsorbent (2g/250ml for GAC) at different initial concentrations of the metal ions of Arsenic ranged from 0.048-1.147 µg/g, cadmium 0.05-2.02 µg/g, copper 10.08-53.62 µg/g, mercury 0.009-0.158 µg/g and lead 13.85 -27.97 µg/g. The contact time was (1-7 hrs), pH 6.5-7.1 and temperature at 28± 1°C were carried out.

3. Experimental

3.1. Instrumentation

Atomic adsorption spectrometer (AAS) 6300 (Shimadzu, Japan) operating with an air acetylene flame was used to analyze the concentration of heavy metals. The pH measurements were performed with a controlled pH analyzer (Systronics).

3.2. Chemicals

Analytical grade reagents were used for heavy metal solution; ACS reagent grade concentrated nitric acid, NaOH and pH buffer solutions (E. Merck) were used to adjusted pH values of samples. In all experimental work, distilled water was used.

3.3. Medicinal plants solution

The medicinal plants are washed, dried in shade and ground into a fine powder (< 0.5 mm) using an analytical laboratory grinder. A weighed amount of plant material is placed in a crucible and ashed by heating in a muffle furnace gradually through different stages. The dried residue is taken in 3% nitric acid warmed filtered and made up to a known volume.

3.4. Adsorbent

Granulated activated carbon was used an adsorbent, the percent heavy metal removal was calculated as

$$\text{Metal ions removal (\%)} = (C_0 - Ce) \times 100 / C_0 \quad (1)$$

Where C_0: initial metal ion concentration of test solution, mg/l;

Ce: final equilibrium concentration of test solution,

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Medicinal plants, part used & Initial Conc of Heavy Metals (ppm)	Time (hrs)	Cu		Cd		As		Pb		Hg	
		Quantity absorbed (ppm)	% absorbed	Quantity absorbed (ppm)	% Absorbed	Quantity absorbed (ppm)	% absorbed	Quantity absorbed (ppm)	% Absorbed	Quantity absorbed (ppm)	% absorbed
Glycyrrhiza glabra (Root)	1	17.48	8.05	1.28	8.57	0.07	7.93	14.30	14.11	0.058	7.99
Cu -19.01	2	13.68	28.04	1.00	28.57	0.06	27.75	11.97	28.11	0.045	27.96
Cd – 1.40	3	9.64	49.29	0.76	45.71	0.04	43.99	9.31	44.08	0.035	44.09
As –0.08	4	6.55	65.54	0.60	57.14	0.03	59.97	8.66	47.99	0.025	60.06
Pb – 16.65	5	4.56	76.01	0.33	76.43	0.02	76.09	4.99	70.03	0.015	75.72
Hg- 0.063	6	1.50	92.11	0.17	87.86	0.01	84.02	3.67	77.96	0.010	84.03
	7	0.50	97.37	0.05	96.43	0.01	92.07	2.30	86.19	0.005	92.01
Plumbago zeylancia	1	34.19	7.99	0.80	13.04	1.06	7.94	15.19	8.49	0.057	7.95
(Root)	2	28.75	22.63	0.66	28.26	0.83	28.01	13.89	16.33	0.044	28.08
Cu -37.16	3	20.81	44.00	0.52	43.48	0.64	43.98	12.25	26.20	0.034	44.32
Cd – 0.92	4	14.86	60.01	0.31	66.30	0.46	60.03	11.40	31.33	0.025	60.06
As –1.15	5	8.91	76.02	0.22	76.09	0.28	76.00	9.96	40.00	0.014	76.95
Pb – 16.60	6	5.94	84.02	0.12	86.96	0.18	84.03	5.64	66.02	0.010	83.94
Hg – 0.062	7	2.08	94.40	0.08	91.30	0.09	92.06	1.32	92.05	0.005	92.05
Salacia Oblonga (Root)	1	21.50	12.07	1.37	8.05	0.04	8.33	14.73	12.48	0.093	7.50
Cu -24.45	2	17.61	27.98	1.07	28.19	0.04	27.08	12.31	26.86	0.072	27.60
Cd – 1.49	3	13.69	44.01	0.80	46.31	0.03	43.75	11.57	31.25	0.054	46.40
As –0.05	4	9.78	60.00	0.59	60.40	0.02	60.42	9.83	41.59	0.041	59.30
Pb – 16.83	5	5.87	75.99	0.35	76.51	0.01	75.83	7.10	57.81	0.024	75.90
Hg – 0.100	6	3.91	84.01	0.23	84.56	0.01	83.96	6.73	60.01	0.016	83.90
	7	1.95	92.02	0.12	91.95	0.00	91.96	2.36	85.98	0.008	92.00
Lannea coromandelica	1	20.28	18.09	0.90	15.89	0.15	8.02	16.34	11.24	0.00	0.00
(Bark)	2	17.82	28.03	0.77	28.04	0.12	28.40	15.14	17.76	0.00	0.00
Cu -24.76	3	13.36	46.04	0.53	50.47	0.09	43.89	13.77	25.20	0.00	0.00
Cd – 1.07	4	9.90	60.02	0.38	64.49	0.06	60.00	12.41	32.59	0.00	0.00
As –0.16	5	5.94	76.01	0.25	76.64	0.04	75.99	9.04	50.90	0.00	0.00
Pb – 18.14	6	3.96	84.01	0.13	87.85	0.03	84.01	5.36	70.89	0.00	0.00
Hg – Not detected	7	1.25	94.95	0.06	94.39	0.01	92.04	2.65	85.61	0.00	0.00

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Table-1 Effect of contact time on the percentage removal of **Heavy Metals (** Cu, Cd, As, Pb & Hg) by Adsorption of Granular activated carbon as adsorbent, **Stirring time: 1-7 hours**-Quantity of activated carbon used: 2/250(g/ml)

Kinetic Adsorption on GAC using Natarajan & khalaf equation

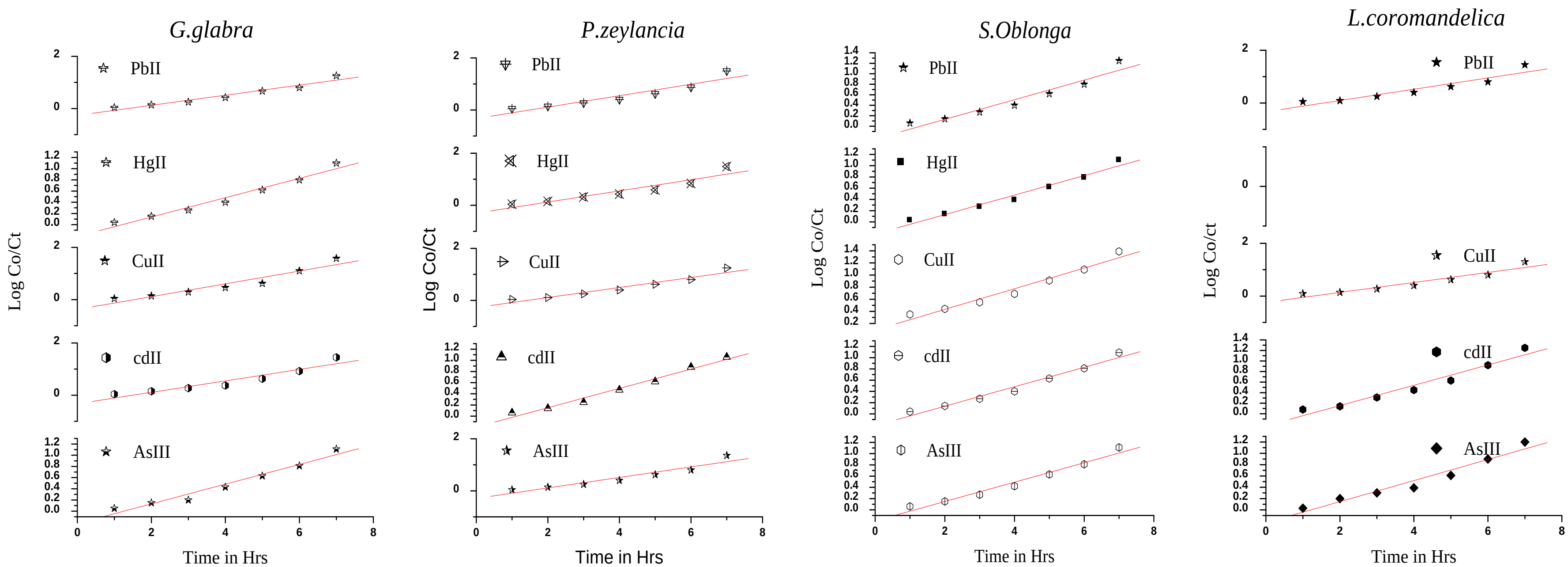


Fig: 1.1 Fig: 1.2 Fig: 1.3 Fig:1.4

Figure: 1.1 – 1.4 Kinetic model for the removal of As (III), Cd(II), Cu(II), Hg(II) & Pb(II) ions by Adsorption on Granulated activated carbon (GAC) using Natarajan & khalaf equation

4.0 KINETIC STUDY

The effect of various experimental parameters like initial concentration of metal ions, contact time, dose of activated carbon and initial pH has been investigated by following batch adsorption technique at 27±1°C. The percentage removal of metal ions increased with the decrease in initial concentration and increase in contact time, dose of adsorbent and initial pH. Adsorption data were modeled with first-order kinetic equations like Natarajan-Khalaf first order equation.

4.1 Rate constant

The rate constant for the adsorption of heavy metal such as As^{3+}, Cd^{2+}, Co^{2+}, Hg^{2+} and Pb^{2+} ions on GAC are calculated using kinetic equations such as Natarajan-khalaf equations . The results shows that the rate constant for the adsorption of heavy metal ions As^{3+}, Cd^{2+}, Co^{2+}, Hg^{2+} and Pb^{2+} ions on GAC was found to be greater. The reason for this may be due to the large surface area and highly active surface sites present in the NPAC than in GAC. The rate of adsorption is higher in GAC.

4.2 Effect of initial concentration

The effect of initial concentration of metal ions on the extent of removal of As^{3+}, Cd^{2+}, Co^{2+}, Hg^{2+} and Pb^{2+} ions by adsorption on activated carbons (GAC) was studied. The relevant data are given in Table 1.

4.3 Effect of contact time

In the adsorption system, contact time plays a vital role, irrespective of the other process parameters affecting the kinetics of adsorption. The effect of contact time on the extent of removal of metal ions was studied. The extent of removal of metal ions increased with the increase in contact time and reached a constant value with the increase in contact time. The relative increase in the extent of removal of As^{3+}, Cd^{2+}, Co^{2+}, Hg^{2+} and Pb^{2+} ions respectively. The optimum contact time at which the maximum removal occurred is fixed as 7 hours for granulated activated carbon and 60 minutes for nano particles of activated carbon for removal of As^{3+}, Cd^{2+}, Cu^{2+}, Hg^{2+} and Pb^{2+} ions.

4.4 Kinetics of adsorption

The kinetics of adsorption of metal ions has been studied by applying the following first order kinetic equations.

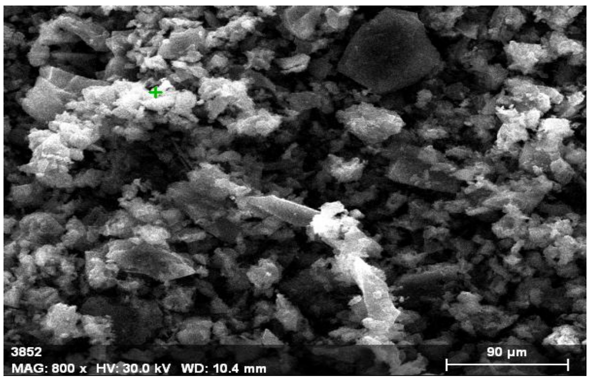
Natarajan and Khalaf equation:

$$\log (Co / C_t) = (k/2.303)t \text{ ---------------(1)}$$

Where Co and Ct are the initial concentration (ppm) and concentration (ppm) of the various time t (min) and (Hrs) respectively, and k is the rate constant of the adsorption. If a plot of log Co/Ct versus t gives a straight line, then the adsorption follows first-order kinetics and the rate constant is computed of the straight line.

5.0 Scanning Electron Microscopy (SEM).

The wide usefulness of carbon is a result of its specific surface area, high chemical and mechanical stability. The chemical nature and pore structure usually determine the sorption activity. High resolution SEM images were made to examine the GAC before and after treated with medicinal plants are given in the figure 5.1 - 5.2. The scanning electron micrographs enable the direct observation of the surface microstructures of the adsorbents. The image of GAC shows well defined particles at 800 x and 5002x with mild agglomeration. It is comparable with the particle size obtained from the Debye-Scherer formula. However, after the adsorption of heavy metals, the surface of the particles is modified and appears to be smooth with some agglomeration.



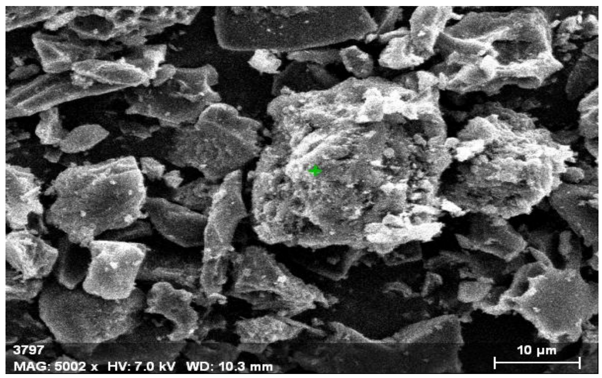


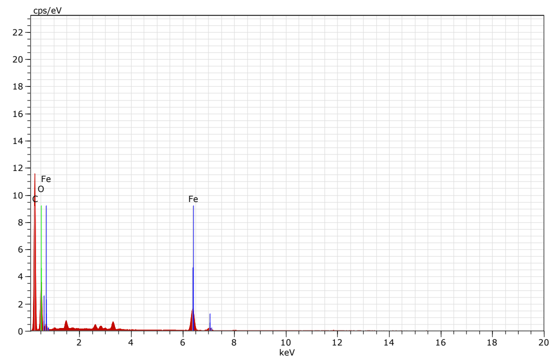
Figure-5.1 Figure-5.2

Figure-5.1.SEM image of Granular activated carbon before adsorption

Figure-5.2 .SEM image of Granular activated carbon after adsorption

5.1 X-ray diffraction studies.

Activated carbon is widely used as an adsorbent due to its high adsorption capacity, high surface area, micro porous structure and high degree of surface respectively. An X-ray energy dispersion analysis (EDX) of the GAC before and after treated with medicinal plants contains heavy metals and the compositions of the heavy metals adsorbed are shown in the fig.5.3 and 5.4. The pattern shows that, the presences of heavy metals are identified



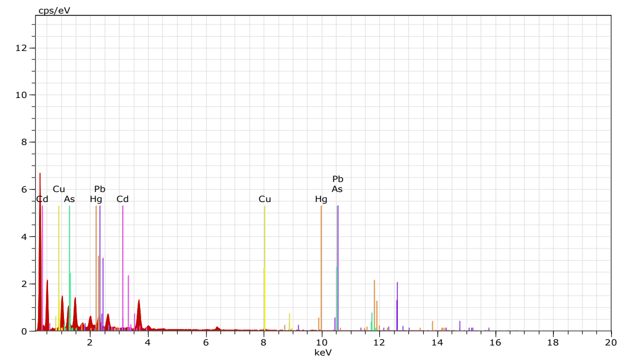


Figure-5.3. Figure-5.4.

Figure-5.3.EDX for Granular activated carbon before adsorption

Figure-5.4.EDX for Granular activated carbon after adsorption

5.3 Results and discussion

On the basis of regression analysis of the experimental data on the adsorptive behaviour of metal ions on activated carbon, it may be inferred that the adsorption behaviour of metal ions on activated carbon is in good agreement with Natarajan and khalf equation.

These can be attributed to three main causes (i) the formation of monolayer coverage on the surface of activated carbon with minimal interaction among molecules of substrate (ii) immobile and localized adsorption and (iii) all sites having equal adsorption energies. The kinetic adsorptions suggest that there are high-energy adsorption sites to favour strong adsorption at low equilibrium concentrations for the activated carbon.

Contact time is effective factor in batch adsorption technique. In order to study the effect of contact time on the removal of theAs^{3+}, Cd^{2+}, Cu^{2+} , Hg^{2+} and Pb^{2+} ions, experiments were conducted at different contact times from 1-7 hrs for Granulated Activated Carbon keeping the optimum concentrations and dosage, pH 6-6.5 and temperature 28 ± 1° C. The variation of the percentage removal of the As^{3+} (96.15%), Cd^{2+} (92.31%), Cu^{2+} (96.71%), Hg^{2+} (92.09%) and Pb^{2+} (94.87%) ions by adsorption of GAC with contact time is shown in tables.

5.4 Conclusion

Granulated activated Carbon nearly 100% adsorptive removal of heavy metal ions under optimized conditions. These experimental on adsorbents would be quite useful in developing an appropriate technology for the removal of heavy metal ions from contaminated medicinal plants.

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