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Chromium (VI) pollution control in waste waters using new bio-sorbents

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ABSTRACT

Powders of leaves and their ashes of *Ficus benghalensis*, *Syzygium cumini*, *Tamarindus indica*, *Acacia nilotica Indica*, *Acacia Arabica* and *Psidium guajava* have been found to have *strong affinity towards Chromium(VI) at low pH values*. The sorption abilities of these bio-products in controlling the Chromium (VI) pollution in waste waters have been studied with respect various physicochemical parameters such as pH, sorption concentration and equilibration time. % of removal of Chromium (VI) is pH sensitive and also depends on sorption concentration and time of equilibration. More than 90% of Chromium (VI) can be removed using these bio-sorbents at pH:2 and at optimum of equilibration time and sorbent concentrations. Cations even in ten fold excess are almost not interfering with the extractability of Chromium at the experimental conditions. Nitrate, Fluoride and Carbonate show seldom interference while sulphate and Phosphate are interfering to *some extent in some sorbets* and moreover even in these, *% of extraction has never come down below 72.0%*; Chloride except in the case of ashes of *Acacia Arabica is not interfering*. The adoptability of the methodologies developed is tested with some real industrial effluents and natural lake samples and found remarkably successful.

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KEYWORDS

Chromium (VI);
Pollution control;
Bio-sorbents;
Applications.

INTRODUCTION

Chromium compounds are widely used in tanning, electroplating, dyeing and textile industries and the effluents discharging from these industries possess Chromium and if proper care is not envisaged in removing, the chromium compounds get in to the nearby water bodies causing pollution problems. Chromium ions being a non-degradable in nature get accumulated in wa-

ter bodies due to bio-amplification and thereby causing environmental threat.

Chromium exists in trivalent and hexavalent states and of these, hexavalent ion is 500 folds more toxic than trivalent ion^[1] and the Chromium (VI) is hazardous to health when its limit in potable waters exceeds 0.05 ppm^[2,3].

Literature survey indicates that much growing interest is being envisaged in developing the methodolo-

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gies to control the Chromium pollution^[4-27]. Researchers developed procedures for the removal of Cr (VI) based on chemical reduction^[4, 5], nanofiltration^[6], bioaccumulation^[7], ion exchange^[8] and adsorption on silica composites^[9, 10]. Activated carbons^[11], Fly Ash^[12], modified zeolites^[13, 14] and bone charcoal^[15] have been explored for the removal of Chromium from waste waters. Ashalatha Singh reviewed the various methods available in literature in removing Chromium from waste waters using microbes^[16]. A number of patents also existing in this regard^[17]. These methods suffer from high cost and are not viable in developing countries and are less encouraging for adoption.

The use of Biomasses or bio-wastes of flora or fauna origin in controlling the pollution either in their native state or chemically modified by evoking their surface sorption phenomenon is another new trend^[18, 28]. In this aspect of research, some agricultural waste materials have been reported as biosorbents for Chromium removal^[19-27].

In the present work, the sorption characteristics of powders of Leaves and their ashes of different plants for Chromium (VI), have been studied with respect to various physicochemical parameters such as pH, time of equilibration and sorbent concentration and we tried to develop simple methodologies in controlling the Chromium (VI) pollution in waste waters by optimizing the extraction conditions.

MATERIALS AND METHODS

(A) Chemicals

All chemicals used were of analytical grade.

1. *Stock solution of Chromium (VI)* was prepared by dissolving 0.144g of A.R. potassium dichromate in double distilled water and is made up to 1 lit. Its concentration is 50ppm. It is suitably diluted as per the need.
2. *Diphenyl carbazide solution*: 0.25g of Diphenyl carbazide was dissolved in 100 ml of 50% of acetone.
3. 6N Sulphuric acid solution was prepared.

(B) Adsorbents

Powders of Leaves and their ashes of various plants were tried for the removal of Chromium from syntheti-

cally prepared polluted waters by optimizing various physicochemical parameters viz., pH, conc. of sorbent and time of equilibration. It has been observed that the Leaves of *Ficus benghalensis*, *Syzygium cumini*, *Tamarindus indica*, *Acacia nilotica Indica*, *Acacia Arabica* and *Psidium guajava* have affinity towards the Chromium (VI) ions.

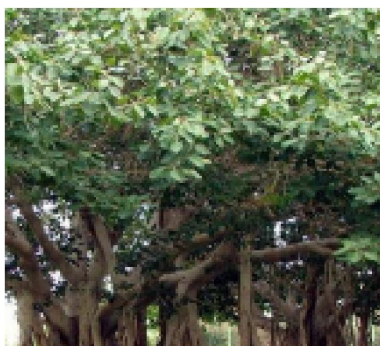
Ficus benghalensis, the banyan, is a large and extensive growing tree of the Indian subcontinent having propagating roots which grow downwards as aerial roots and once these roots reach the ground, they grow into woody trunks that can become indistinguishable from the main trunk. It belongs to Moraceae family. *Syzygium cumini* is an evergreen tropical tree in the flowering plant family of Myrtaceae and have traditional medicinal uses. *Tamarindus indica* is a long-lived tropical evergreen tree with a spreading crown and feathery evergreen foliage and fragrant flowers yielding hard yellowish wood and long pods with edible chocolate-colored acidic pulp and it belongs to Fabaceae family and is cultivated in tropical regions. *Acacia nilotica Indica* is one of the species of acacia belongs to Fabaceae and is a medium sized deciduous tree with crooked and forked trunk and is grown well in South Asia. *Acacia Arabica* is the gum-Arabic tree of India and possesses traditional medicinal values and it belongs to Fabaceae family. The *Psidium guajava* is an evergreen shrub or small tree widely cultivated in tropical and subtropical regions around the world and it belongs to Myrtaceae family.

The Leaves of *Ficus benghalensis*, *Syzygium cumini*, *Tamarindus indica*, *Acacia nilotica Indica*, *Acacia Arabica* and *Psidium guajava* were cut, washed with tap water followed by distilled water and then sun dried. The dried materials were powdered to a fine mesh of size: <75 μ and activated at 105°C in an oven and then employed in this study. Further, these leaves were burnt to ashes and these ashes were also used in this work.

(C) Adsorption experiment

Batch system of extraction procedure was adopted^[28-30]

Carefully weighted quantities of adsorbents were taken into previously washed 1 lit/500 ml stopper bottles containing 500ml/250ml of Potassium Dichromate so-

*Ficus benghalensis**Syzygium cumini**Tamarindus indica**Acacia nilotica Indica**Acacia Arabica**Psidium guajava*

lution of predetermined concentrations. The various initial pH values of the suspensions were adjusted with dil HCl or dil NaOH solution using pH meter. The samples were shaken vigorously in mechanical shakers and were allowed to be in equilibrium for the desired time. After the equilibration period, an aliquot of the sample was taken for Chromium determination. Chromium (VI) was determined Spectrophotometrically by using "Diphenyl Carbazide" method^[31].

Estimation of chromium (VI)

An aliquot amount of Chromate sample was taken in a 50ml volumetric flask. To it 1ml of 6N Conc. H_2SO_4

solution and 1ml of Diphenyl Carbazide solution were added successively and the solution was then diluted to the volume and mixed well. Then O.D. of the developed color was measure against blank at 540 nm using U.V. and Visible Spectrometer.

Thus obtained O.D Value was referred to a standard Graph (drawn between O.D and Concentration) prepared with known amounts of Chromium by adopting the method of Least Squares to find concentration of Chromium in unknown solutions.

The sorption characteristics of the said adsorbents were studied with respect to the time of equilibration,

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TABLE 1 : Effect of interfering Ions on the Extractability of Chromium (VI) with different Bio-sorbents:

| S.No | Adsorbent and its concentration | Maximum Extractability at optimum conditions | Extractability of Chromium (VI) in presence Ten fold excess of (500ppm) interfering ions at optimum conditions: Conc. of Chromium(VI): 50 ppm | | | | | | | | | | |
|------|---|--|---|-------------------------------|-----------------|-------------------------------|----------------|-------------------------------|------------------|------------------|------------------|------------------|------------------|
| | | | SO ₄ ²⁻ | NO ₃ ²⁻ | Cl ⁻ | PO ₄ ³⁻ | F ⁻ | CO ₃ ²⁻ | Ca ²⁺ | Mg ²⁺ | Cu ²⁺ | Zn ²⁺ | Ni ²⁺ |
| 1 | Powder of Ficus benghalensis leaves: 2.5 gms/lit | 94.2%; pH:2, 3.0hrs | 92.0% | 93.2% | 93.2% | 72.1% | 93.1% | 92.4% | 95.6% | 94.0% | 90.0% | 88.0% | 90.1% |
| 2 | Powder of Syzygium cumini leaves 2.0gms/lit | 91.0% pH:2, 2.0 hrs | 89.1% | 90.1% | 91.0% | 88.1% | 89.0% | 88.0% | 83.1% | 90.0% | 90.5% | 90.0% | 89.0% |
| 3 | Powder of Tamarindus indica leaves; 3.0 gms/lit | 90.2% pH:2., 2.5 hrs | 87.2% | 89.1% | 87.2% | 90.0% | 87.0% | 86.1% | 90.1% | 89.6% | 86.0% | 83.1% | 86.2% |
| 4 | Powder of Acasia nolitica Indica leaves;2.5 gms/lit | 90.8% pH:2, 3.0 hrs | 79.1% | 90.1% | 89.2% | 88.0% | 90.0% | 88.3% | 89.0% | 89.0% | 90.1% | 89.0% | 89.3% |
| 5 | Powder of Acasia Aribica leaves ;3.0 gms/lit | 89.0% pH:2, 2.5 hrs | 81.0% | 89.0% | 88.0% | 74.1% | 87.2% | 85.4% | 82.1% | 88.1% | 88.0% | 87.2% | 88.5% |
| 6 | Powder of Psidium leaves; 2.0 gms/lit | 97.0% pH:2, 3.0 hrs | 92.1% | 97.0% | 96.2% | 72.1% | 96.0% | 94.2% | 96.1% | 89.8% | 92.1% | 95.5% | 96.5% |
| 7 | Ashes of Ficus benghalensis leaves: 2.0 gms/lit | 96.0%; pH:2, 2.5 hrs | 72.1% | 94.0% | 95.0% | 86.0% | 90.2% | 94.0% | 92.0% | 93.5% | 95.0% | 90.9% | 92.0% |
| 8 | Ashes of Syzygium cumini leaves;1.5 gms/lit | 92.5% pH:2, 2.0 hrs | 84.2% | 90.0% | 91.2% | 84.1% | 82.4% | 91.0% | 90.1% | 91.5% | 84.0% | 91.2% | 93.4% |
| 9 | Ashes of Tamarindus indica is leaves;2.5 gms/lit | 93.0% pH:2, 2.0hrs | 92.2% | 91.2% | 92.1% | 72.1% | 87.1% | 89.6% | 90.8% | 92.1% | 90.0% | 92.0% | 92.1% |
| 10 | Ashes of Acasia indica leaves; 2.0 gms/lit | 92.8%; pH:2; 2.0 hrs | 90.1% | 92.0% | 92.1% | 80.0% | 89.0% | 88.7% | 91.6% | 91.6% | 87.0% | 91.5% | 86.2% |
| 11 | Ashes of Acasia Aribica leaves ;2.5 gms/lit | 92.0% pH:2, 2.5 hrs | 90.2% | 89.0% | 82.0% | 86.0% | 90.0% | 86.0% | 86.7% | 84.0% | 90.0% | 91.0% | 91.9% |
| 12 | Ashes of Psidium leaves; 1.5 gms/lit | 99.0%, pH:2, 2.5 hrs | 94.0% | 96.0% | 98.1% | 76.0% | 92.1% | 94.0% | 93.1% | 96.0% | 98.2% | 97.2% | 96.8% |

pH and sorbent dosage. At a fixed sorbent concentration, the % removal of Chromate was studied with respect to time of equilibration at various pH values. The results obtained were presented in the Graph Nos. A:

1-12 and B: 1&2. To fix the minimum dosage needed for the maximum removal of the Chromate ions for a particular sorbent at optimum pH and equilibration times, extraction studies were made by studying the % of

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TABLE 2 : Extractability of Chromium in Different Industrial Effluents and Natural Lake Samples using Bio-sorbents

| Bio-Sorbent | % of Extractability of Chromium(VI) in diverse Samples (actual Conc. of Chromate is shown in parenthesis) | | | | | | | | |
|--|---|------------------------|------------------------|-----------------------------------|------------------------|-----------------------|----------------------|----------------------|----------------------|
| | Tannery Industry effluents | | | Chrome plating Industry effluents | | | Natural Lake Samples | | |
| | Sample-1 (12.5 ppm) | Sample-2 (21.5 ppm) | Sample-3 (14.5 ppm) | Sample-4 (21.5ppm) | Sample-5 (24.5 ppm) | Sample-6 (15.8ppm) | Sample-7 (15 ppm) | Sample-8 (20 ppm) | Sample-9 (25 ppm) |
| Leaves powder of Ficus benghalensis. :at pH:2; Equilibration time: 3.0 hrs and sorbent concentration: 2.5 gm/lit | 82.6% | 87.2% | 84.6% | 81.8% | 86.3% | 91.4% | 88.7% | 90.5% | 85.9% |
| Leaves powder Syzygium cumini. at pH:2; Equilibration time: 2.0 hrs and sorbent concentration: 2.0 gm/lit | 81.3% | 80.6% | 79.5% | 80.2% | 83.3% | 85.4% | 82.9% | 81.2% | 86.4% |
| Leaves powder of Tamarindus indica. :at pH:2; Equilibration time: 2.5 hrs and sorbent concentration: 3.0 gms/lit | 70.4% | 72.6% | 74.5% | 74.9% | 76.2% | 79.1% | 80.2% | 82.9% | 84.6% |
| Leaves powder of Acasia nolitica Indica. :at pH:2; Equilibration time: 3.0 hrs and sorbent concentration: 2.5 gm/lit | 72.6% | 70.4% | 69.4% | 62.3% | 70.9% | 68.5% | 66.7% | 69.3% | 68.2% |
| Leaves powder of Acasia Aribica. :at pH:2; Equilibration time: 2.5 hrs and sorbent concentration: 3.0 gms/lit | 73.2% | 74.6% | 76.6% | 72.3% | 74.1% | 80.2% | 79.9% | 81.1% | 77.4% |

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| | Tannery Industry effluents | | | Chrome plating Industry effluents | | | Natural Lake Samples | | |
| | Sample-1 (12.5 ppm) | Sample-2 (21.5 ppm) | Sample-3 (14.5 ppm) | Sample-4 (21.5ppm) | Sample-5 (24.5 ppm) | Sample-6 (15.8ppm) | Sample-7 (15 ppm) | Sample-8 (20 ppm) | Sample-9 (25 ppm) |
| Leaves powder of Psidium. at pH:2; Equilibration time: 3.0 hrs and sorbent concentration: 2.0 gm/lit | 91.4% | 89.4% | 92.4% | 90.6% | 88.2% | 90.6% | 88.7% | 86.2% | 84.3% |
| Ashes of Leaves of Ficus benghalensis. :at pH:2; Equilibration time: 2.5 hrs and sorbent conc.: 2.0 gms/lit | 86.3% | 90.1% | 92.7% | 93.4% | 89.1% | 92.3% | 94.1 % | 94.7% | 92.6% |
| Ashes of Leaves powder Syzygium cumini. :at pH:2; Equilibration time: 2.0 hrs and sorbent concentration: 1.5 gm/lit | 91.4% | 90.8% | 88.3% | 89.4% | 86.2% | 90.1% | 87.6% | 89.2% | 91.9% |
| Ashes of Leaves powder: Tamarindus indica. at pH:2; Equilibration time: 2.0 hrs and sorbent concentration: 2.5 gm/lit | 72.4% | 80.1% | 81.3% | 88.5% | 89.4% | 90.0% | 90.6% | 91.2% | 91.9% |
| Ashes of Leaves powder :Acacia nolitica.indica :at pH:2; Equilibration time: 2.0 hrs and sorbent conc.: 2.0 gm/lit | 72.4% | 86.9% | 85.3% | 87.3% | 83.2% | 88.6% | 89.4% | 89.9% | 79.4% |
| Ashes of Leaves powder of Acasia Aribica : at pH:2; Equilibration time: 2.5 hrs and sorbent conc. 2.5 gm/lit | 76.3% | 84.6% | 83.7% | 90.2% | 91.4% | 91.9% | 88.4% | 89.6% | 90.9% |
| Ashes of Leaves powder of Psidium. :at pH:2; Equilibration time: 2.5 hrs and sorbent concentration: 1.5 gm/lit | 79.4% | 87.6% | 88.4% | 90.5% | 92.5% | 91.3% | 92.7% | 90.9% | 89.5% |

extraction with respect to the sorbent dosage. The results obtained were presented in the Graph Nos. C: 1 & 2.

(D) Effect of interfering ions

The interfering ions chosen for study are the common ions present in natural waters, viz., Sulphate, Nitrate, Phosphate, Fluorides, Carbonate, Chloride, Calcium, Magnesium, Copper, Zinc and Nickel. The syn-

thetic mixtures of Chromium (VI) and one of the interfering ions were so made that the concentration of the interfering ions maintained at *ten fold excess than the Chromium (VI) ion concentration*. 500 ml of these solutions were taken in stopped bottles and then correctly weighed optimum quantities of the promising sorbents were added. Optimum pH was adjusted with dil. HCl or dil. NaOH using pH meter. The samples were

shaken in shaking machines for the desired optimum periods and then the samples were filtered and analyzed for Chromium (VI). % of extraction was calculated from the data obtained. The results are presented in the TABLE No. 1.

(E) Applications of the developed bio-sorbents

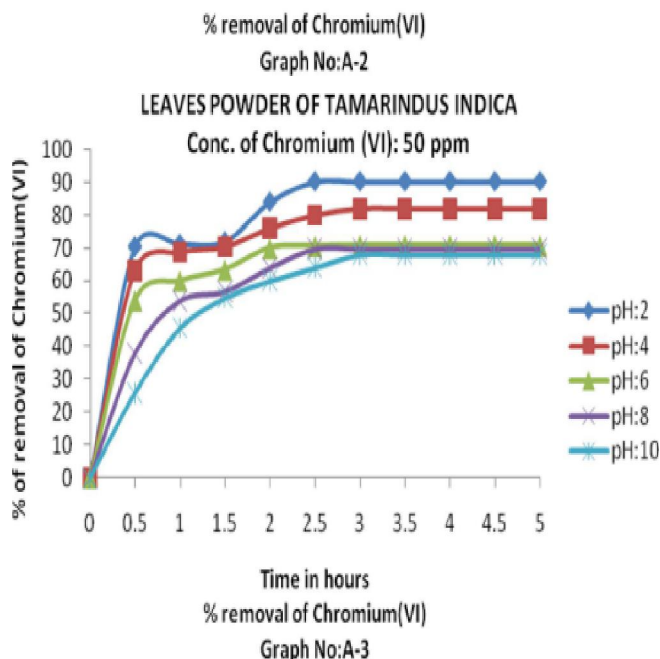
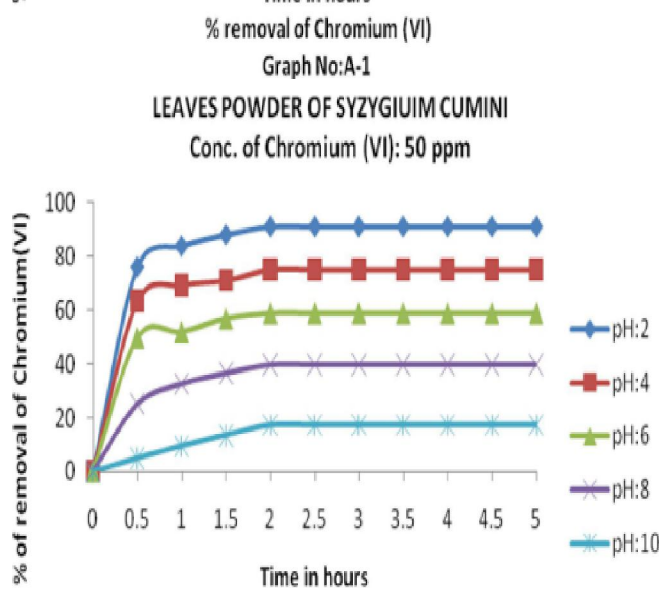
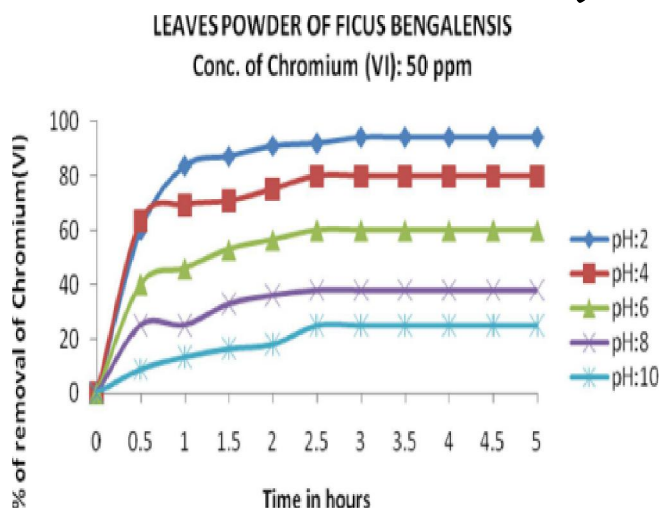
The adoptability of the methodology developed with the new bio-sorbents in this work for removing Chromium (VI) is tried with some real sewage/effluent samples of some industries. For this purpose, three samples were collected from tannery industries in Hyderabad and three from Chrome plating industries in Chennai and these samples were analyzed for the actual concentration of Chromium (VI). Further, three more natural samples from three lakes at different places in Bapatla mandalam of Guntur Dt of Andhra Pradesh were collected and these sample were fed with known amounts of Chromium (VI).

Then these samples were subjected to extraction for Chromium (VI) using the bio-sorbents developed in this work at optimum conditions of pH, equilibration time and sorbent concentration. The results obtained were presented in the TABLE 2.

RESULTS AND DISCUSSION

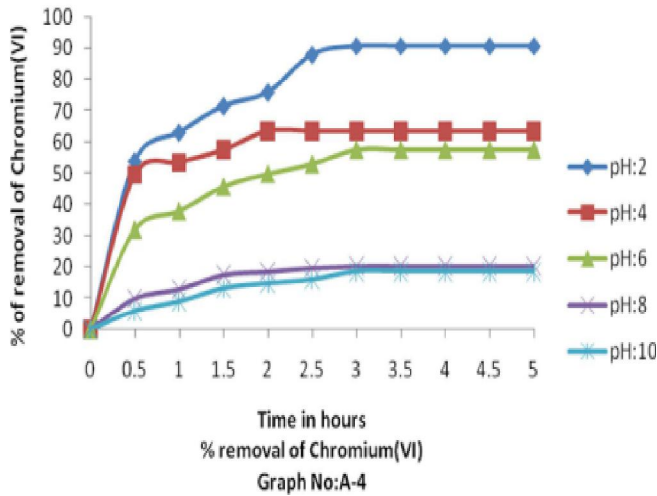
Leaves and their ashes of *Ficus benghalensis*, *Syzygium cumini*, *Tamarindus indica*, *Acacia nilotica*, *Acacia Arabica* and *Psidium guajava* have been found to have affinity towards the Chromium (VI) ions. The extractability of Chromium has been studied with respect to various physicochemical parameters such as pH, time of equilibration and sorption concentration and the results obtained are presented in the Graph No. A: 1-12; B: 1 & 2; C: 1&2). The following observations are significant:

1. *Time of equilibration*: Percent of extractability increases with time for a fixed adsorbent at a fixed pH and after certain duration, the extractability remains constant, i.e. an equilibrium state has been reached. In other words, there will not be any further adsorption after certain time of equilibration time (vide Graph Nos. A: 1-6). As for example, in the case of *Ficus benghalensis*, at pH:2, % of extraction is 60.0% at 0.5 hrs, 83.6% at 1.0 hr,

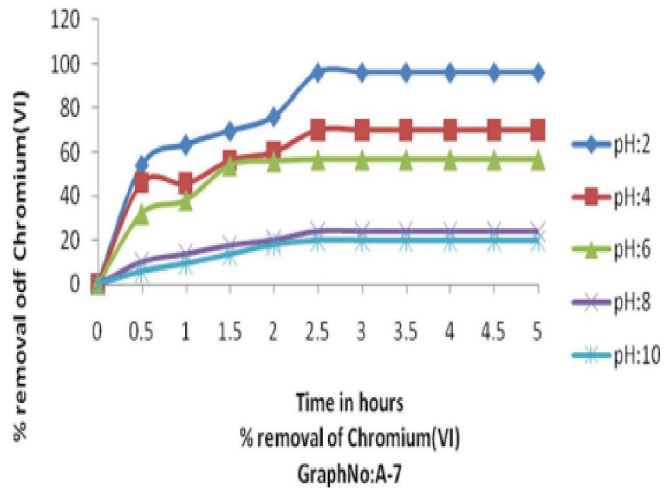


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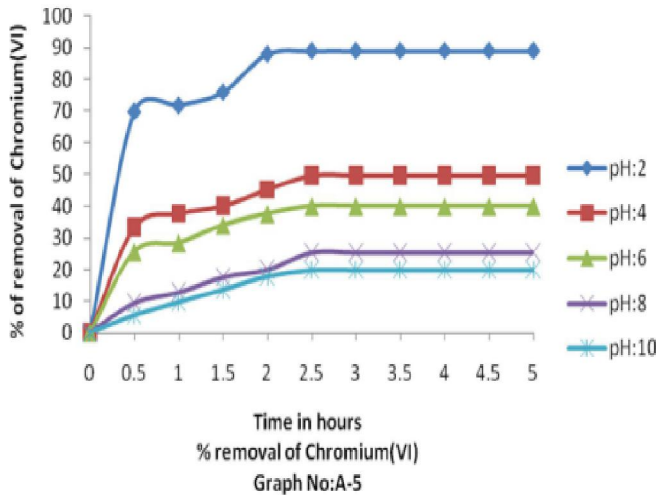
LEAVES POWDER OF ACASIA INDICA
Conc. of Chromium (VI): 50 ppm



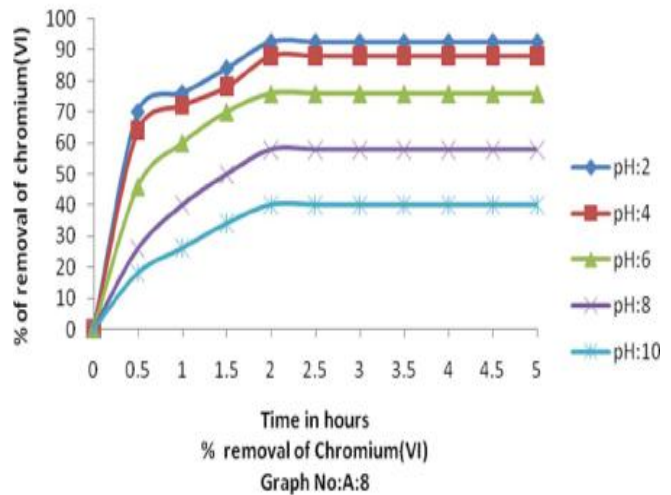
ASHES OF FICUS BENGALENSIS LEAVES
Conc. of Chromium(VI):50PPM



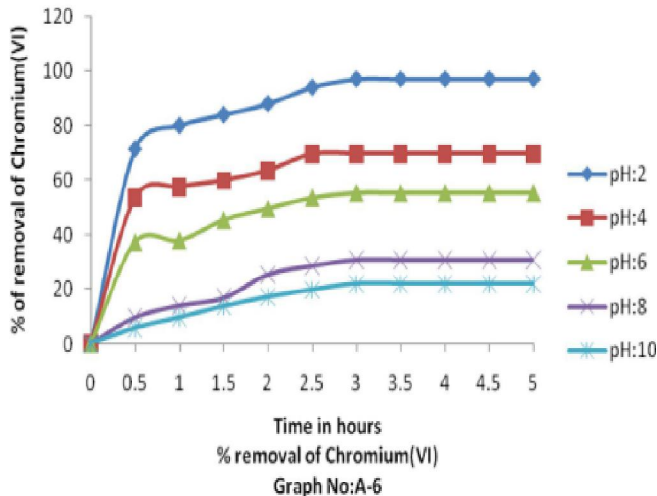
LEAVES POWDER ACASIA ARABICA
Conc. of Chromium (VI): 50 ppm



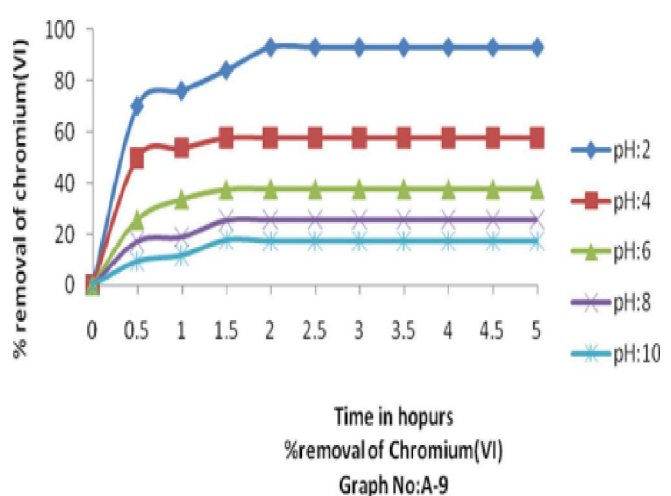
ASHES OF SYZYGIUM CUMINI LEAVES
Conc. of Chromium(VI) : 50 ppm

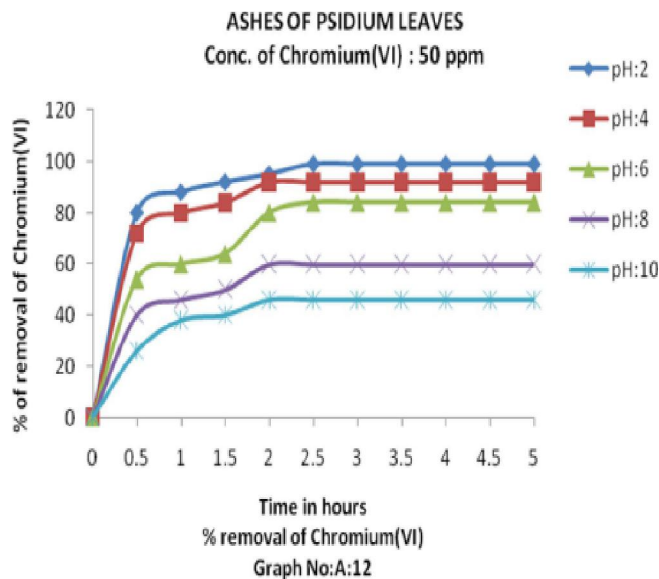
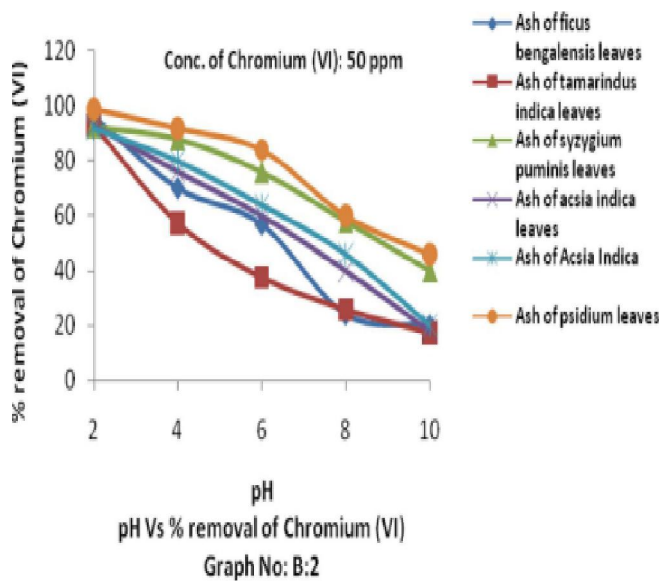
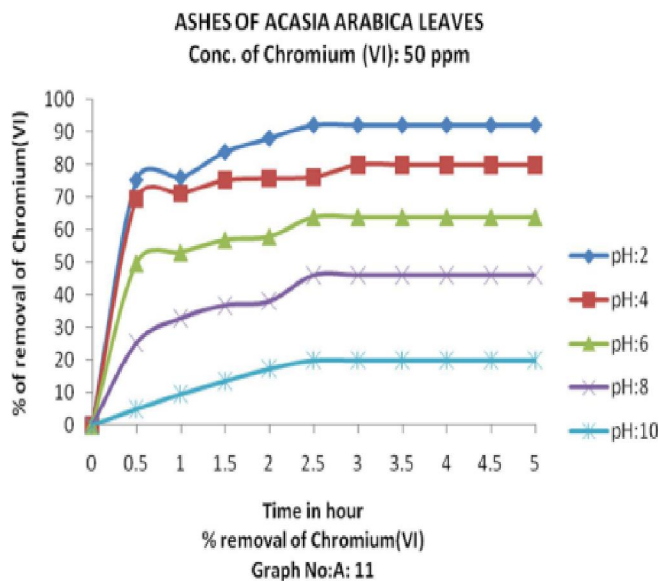
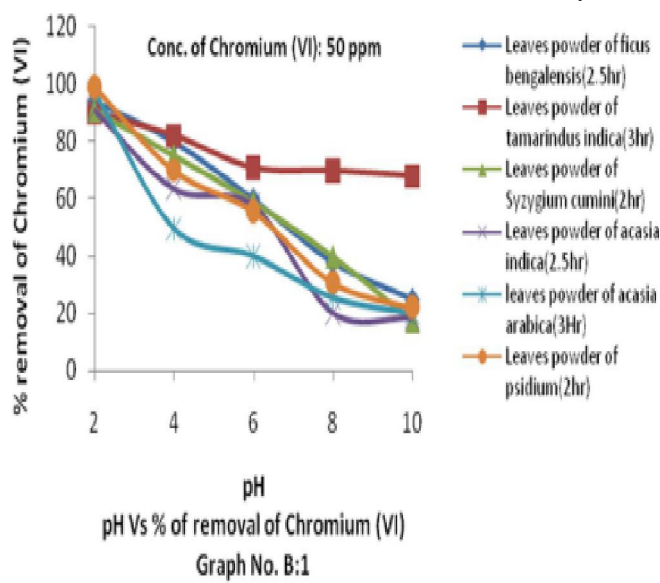
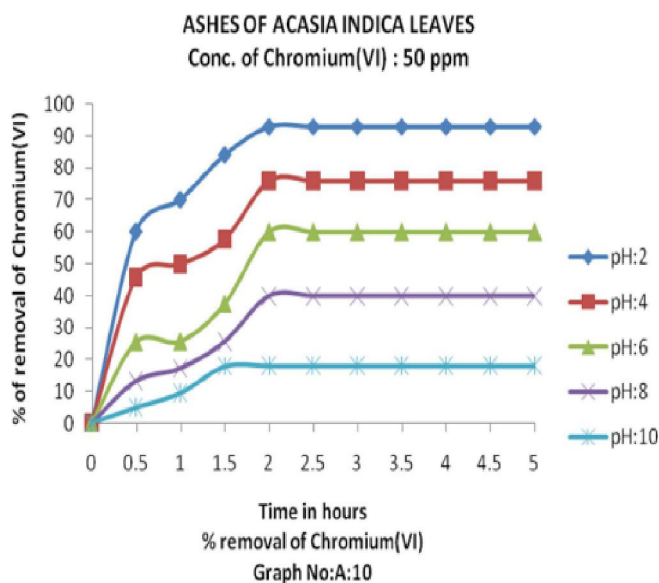


LEAVES POWDER OF PSIDIUM
Conc. of Chromium (VI): 50 ppm



ASHES OF TAMARINDUS INDICA LEAVES
Conc of Chromium(VI):50ppm

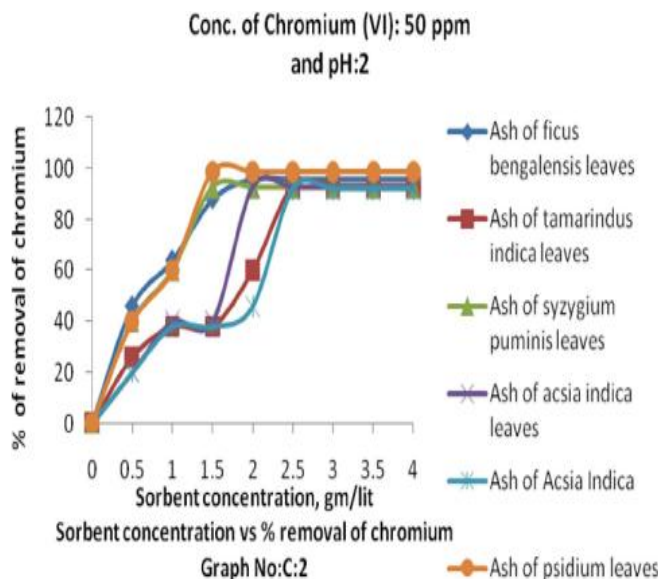
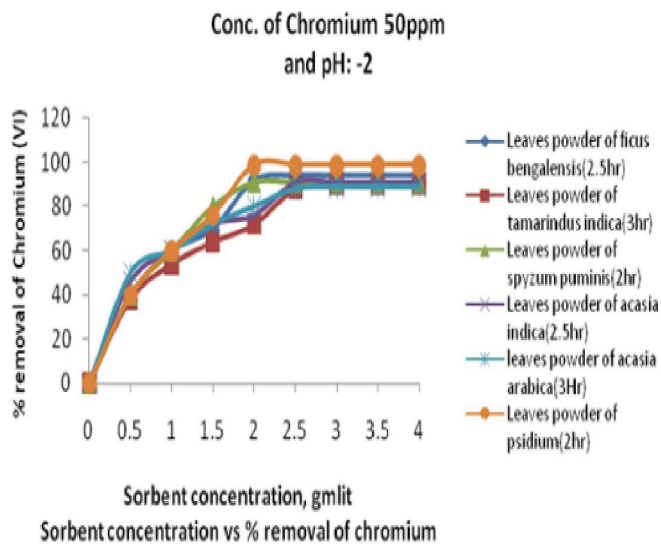




87.2% at 1.5 hrs, 91.0% at 2.0 hrs, 92.0% at 2.5 hrs, 94.2% at 3 hrs and 94.2% above 3 hrs.(vide Graph No.A:1). The same trend is noticed in the case of other sorbents.

2. *pH*: % of extraction is found to be *pH sensitive*. As *pH* decreases, % of extraction is found to be increasing (Vide Graph: B: 1 and 2). As for example, with the powder of *Ficus benghalensis* leaves, % of extractability is found to be 25.0% at *pH*:10; 38.0% at *pH*:8; 60.0% at *pH*:6; 80.0% at *pH*:4 and 94.2% at *pH*: 2 while with the ashes of *Ficus benghalensis* leaves % of extractability is found to be: 20.0% at *pH*:10, 24.2% at *pH*:8, 56.8% at *pH*:6, 70.0% at *pH*:4 and 96.0% at *pH*:2. Similar trend is found in the case of other sorbents:

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at pH:2,4,6,8 and 10 respectively, extractability of Chromium(VI) is found to be 91.0%, 75.2%, 59.0%, 40.0% and 17.4% in the case of powder of *Syzygium cumini* leaves after 2 hrs of equilibration time; 90.2%, 82.0%, 70.8%, 69.8% and 68% in the case of powder of leaves of *Tamarindus indica* after 2.5 hrs of equilibration; 90.8%, 63.6%, 57.8%, 20.4% and 18.6% in case of powder of leaves of *Acacia nilotica Indica* after 3 hrs of equilibration; 89.0%, 49.6%, 40.0%, 25.4% and 20.0% in case of powder of leaves of *Acacia Arabica* after 2.5 hrs of equilibration time; 97.0%, 69.8%, 55.6%, 30.8%, and 22.0% in case of powder of leaves of *Psidium guajava* after 3 hrs of equilibration time.

In the case of ashes of *Syzygium cumini*, 92.5%, 88.0%, 76.0%, 59.0% and 40.0% have been found at pH: 2, 4, 6, 8 and 10 respectively at an equilibration period of 2 hrs; 93.0%, 57.4%, 37.6%, 25.8% and 17.4% at equilibration time of 2 hrs in the case of ashes of *Tamarindus indica* leaves; 92.0%, 76.0%, 60.0%, 40.0% and 18.0% at equilibration time of 2 hrs with ashes of *Acacia nilotica Indica*; 92.8%, 76.0%, 64.0%, 46.0% and 20.0% at equilibration time of 2.5 hrs with ashes of *Acacia Arabica*; 99.0%, 92.0%, 84.0%, 60.0% and 46.0% at equilibration time of 2.5 hrs with ashes of *Psidium guajava*.

3. The maximum % of extractability is found to be marginally more with ashes of leaves than with raw powders of leaves.
4. In most of the sorbents, time of equilibration needed for maximum extractability of Chromate is found to be less for ashes than with the raw powder of leaves. With leaves powders of *Ficus benghalensis*, *Syzygium cumini*, *Tamarindus indica*, *Acacia nilotica Indica*, *Acacia Arabica* and *Psidium guajava*, the equilibration time needed for maximum extraction is found to be 3 hrs, 2 hrs, 2.5 hrs, 3 hrs, 2.5 hrs and 3.0 hrs respectively at optimum pH:2 while with their ashes, the optimum equilibration times are found to be 2.5 hrs, 2.0 hrs, 2.0 hrs, 2.0 hrs, 2.5 hrs and 2.5 hrs. respectively (vide Graph Nos. A:1-12).
5. **Sorbent Concentration:** The sorbent dosage needed for maximum extraction of Chromate is found to be less in the case of leaves powders than with their ashes. Sorbent concentration for maximum extraction at optimum conditions of pH and equilibration is found to be 2.5 gram/lit for the powders of leaves of *Ficus benghalensis* while with its ashes optimum sorption concentration has been reduced to 2.0 gms/lit. Similarly, with the powders of leaves of *Syzygium cumini*, optimum sorbent concentration is 2.0 gm/lit but with their ashes, 1.5 gm/lit is sufficient. In the case of powders of leaves of *Tamarindus indica*, *Acacia nilotica Indica*, *Acacia Arabica* and *Psidium guajava*, the sorbent concentration needed is found to be 3.0 gms/lit, 2.5 gms/Lit, 3.0 gms/lit and 2.0 gms/lit respectively while with their ashes 2.5 gms/lit, 2.0 gm/lit, 2.5 gm/lit

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and 1.5 gms/lit. respectively are sufficient. (Vide Graph No.C:1 and 2).

6. The % of maximum extractability of Chromium (VI) at optimum conditions of pH and equilibration time are found to be 94.2%, 91.0%, 90.2%, 90.8%, 89.0% and 97.0% in the case of powders of leaves of *Ficus benghalensis*, *Syzygium cumini*, *Tamarindus indica*, *Acacia nilotica* Indica, *Acacia Arabica* and *Psidium guajava* respectively (vide Graph Nos.A:1-6).
7. With ashes of *Ficus benghalensis*, *Syzygium cumini*, *Tamarindus indica*, *Acacia nilotica* Indica, *Acacia Arabica* and *Psidium guajava*, % of maximum extractability is found to be 96.0%, 92.5%, 93.0%, 92.8%, 92.0% and 99.0% respectively at optimum conditions of pH: 2 and equilibration times of 2.5 hrs, 2.0 hrs, 2.0 hrs, 2.0 hrs, 2.5 hrs and 2.5 hrs respectively (vide Graph Nos.A: 7-12).
8. Interfering Ions: The extractability of Chromate ions in presence of ten fold excess of common ions found in natural waters, namely, Sulphate, Nitrate, Chloride, Phosphate, Fluoride, Carbonate, Calcium, Magnesium, Copper, Zinc and Nickel ions, has been studied. The results are presented in TABLE No. 1.
 - Cations envisaged marginal effect on the % extractability of Chromate with the sorbents of the present work at the optimum conditions of time of equilibration, pH and sorbent concentration. % of extractions of Chromate is found to be between 88.0% to 95.6% with leaves powder of *Ficus benghalensis* and 90.9% to 95.0% with its ashes; 83.1% to 90.5% with leaves powder of *Syzygium cumini* and 84.0% to 93.4% with its ashes; 83.1% to 90.1% with leaves powder of *Tamarindus indica* and 90.0% to 92.1% with its ashes; 89.0% to 90.1% with leaves powder of *Acacia nilotica* Indica and 86.2% to 91.6% with its ashes; 82.1% to 88.5% with leaves powder of *Acacia Arabica* and 84.0% to 91.9% with its ashes; and 89.8% to 96.5% with leaves powder of *Psidium guajava* and 93.1 to 98.2%.
 - Anions:
 - SO_4^{2-} is found to be interfering to some extent only with the powder of leaves of *Acacia nilotica* Indica

and *Acacia Arabica* and also in the case of ashes of leaves of *Ficus benghalensis* (vide S. No. 4,5 and 7 of TABLE Nos:1) and in the rest of the sorbents, the extractability of Chromates is seldom effected.

- Ten fold excess of NO_3^- , Fluoride and Carbonate are not interfering with the % of extractability of Chromate in all the sorbents of interest.
- Chloride even in ten fold excess is not interfering with the extractability of Chromate in all sorbents of study except in the case of ashes of *Acacia Arabica* (vide 5th Column of TABLE No. 1)
- Phosphate is found to be interfering the extraction with respect to the sorbents: leaves powders of *Ficus benghalensis*, *Acacia Arabica* and *Psidium guajava* and also with the ashes of *Tamarindus indica* and *Psidium guajava*. However, the extractability never comes down below 72.1%. In the remaining sorbents, the % of extractability is almost un-effected (Vide 6th column of TABLE No. 1)

APPLICATIONS

The Applicability of the methodologies developed in this work have been tested with respects to the real samples of diverse nature, collected from the sewages/effluents of Tannery and Chrome plating industries and also in natural lakes. The results have been presented in the TABLE No: 2.

It is found that the sorbents developed in this work are successful in removing Chromates at optimum conditions of pH, equilibration time and sorbent dosage. % removal of Chromates is found to be: 81.8% to 91.4% with leaves powder of *Ficus benghalensis* and 86.3% to 94.7% with their ashes; 79.5% to 86.4% with leaves powder of *Syzygium cumini* and 86.2% to 91.9% with their ashes; 70.4% to 84.6% with the leaves powder of *Tamarindus indica* and 72.4% to 91.9% with their ashes; 62.3% to 72.6% with the leaves powder of *Acacia nilotica* Indica and 72.4% to 89.9% with their ashes; 72.3% to 81.1% with leaves powder of *Acacia Arabica* and 76.3% to 91.9% with their ashes; 84.3% to 92.4% with the leaves powder of *Psidium guajava* and 79.4% to 92.7% with their ashes.

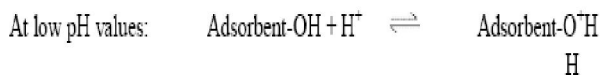
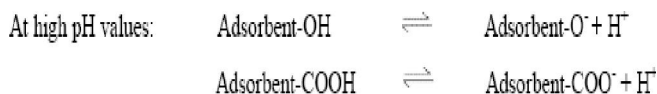
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DISCUSSIONS

The available data is inadequate to propose sound theoretical explanations for each observation made as it needs surface studies of “adsorbent and adsorbate interactions” using more sophisticated instruments and methodologies and it is beyond the aims of this work.

However, the observations may be accounted as follows:

- The bio-sorbents may be having some natural compounds which have affinity towards Chromate at low pH values.
- Further, these natural substances have -OH/COOH groups and their dissociation is pH dependent and this imparts weak anion exchange ability at low pH values and weak cation exchange ability at high pH values as per the equilibrations:



- In basic solutions, the hexavalent Chromium presents as tetrahedral Chromate ions CrO_4^{2-} , between pH: 2 to 6, the species: HCrO_4^- and the orange red dichromate ions $\text{Cr}_2\text{O}_7^{2-}$ are in equilibrium and at pH values less than 1, the main species is H_2CrO_4 .
- So, Chromate being an anion in the pH range: 2-6, is get sorbed by the leaves materials at low pHs due to weak anion exchange nature and thus results in higher % of removal at low pH values.. As pH increases, the cation exchanging nature prevails and this results in low % removal of Chromate ions.
- Further, these natural materials may have of metal ions like Ca, Mg, Cu, Zn, Fe, Al. and these di/trivalent metal ions form sparingly soluble salts with of Chromate which are gelatinous in nature and are being trapped in the matrixes of the bio-adsorbents and thus resulting in the increase of % removal of Chromate. This is more so in the case of ashes as adsorbents, which are oxides of some metal ions.
- Ashes are the oxides of some heavy metals containing large amounts of silica. The ashes, contains ‘-

OH’ groups and ‘-O-’. The observed behaviors of increase in extractability with the decrease in pH may be understood in the same lines as described in the case of raw powders of leaves. In fact, the transition pH for silica from anion exchanging nature to cation exchanging nature is 3^[32-34] and this supports the proposed logic for the observed behavior.

- The decrease in the rate of adsorption with the progress in the equilibration time may be due to the more availability of adsorption sites initially and are progressively used up with time due to the formation of adsorbate (Chromate) film on the active sites of adsorbent and thus resulting in decrease in capability of the adsorbent.
- The observations made with respect to the foreign ions are also confirming as per the expected nature of extraction. % of extractability is less affected even in the presence of ten fold excess of cations chosen for study but some interference to some extent is found with some anions especially Sulphate and Phosphate.

CONCUSSIONS

1. Powders of leaves of *Ficus benghalensis*, *Syzygium cumini*, *Tamarindus indica*, *Acacia nilotica* Indica, *Acacia Arabica* and *Psidium guajava* have been found to have strong affinity towards Chromate at low pH values.
2. % of removal of Chromate is pH sensitive and also depends on sorption concentration and time of equilibration
3. The conditions for the maximum extraction of Chromate at minimum dosage and equilibration time have been optimized.
4. Sorbent dosage and time needed for the maximum removal of Chromate is less for the ashes of leaves than with the raw leaves powders.
5. Ten fold excess of common cation ions present in natural waters, viz., Ca^{2+} , Mg^{2+} , Cu^{2+} , Zn^{2+} and Ni^{2+} have less affected the % of extraction of Chromate at optimum conditions of pH, equilibration time and sorbent concentration. Nitrates, Fluoride and Carbonate even when present in ten fold excess has showed almost ‘no’ interference with all the bio-sorbent. Ten fold excess of Sulphates and Phos-

phates in few sorbents have showed interference to some extent but however, the extraction *has never come down below 72.1%*. Chloride, except in the case of ashes of *Acacia Arabica*, has showed seldom interference.

6. We claim 94.2%, 91.0%, 90.2%, 90.8%, 89.0% and 97.0 % of removal of Chromate from synthetic waters with the leaves powders of *Ficus benghalensis*, *Syzygium cumini*, *Tamarindus indica*, *Acacia nilotica Indica*, *Acacia Arabica* and *Psidium guajava* respectively at pH:2 and at optimum of equilibration time and optimum sorbent concentrations. The % of removal is found to be 96.0%, 92.5%, 93.0%, 92.8%, 92.0% and 99.0% in the case ashes of *Ficus benghalensis*, *Syzygium cumini*, *Tamarindus indica*, *Acacia nilotica Indica*, *Acacia Arabica* and *Psidium guajava* respectively at pH 2 and at optimum conditions of equilibration time and sorbent concentration.
7. The suitability of the developed methodologies in this work is tested with respect to diverse waste water samples collected in nine different places. The developed methods have been found to be remarkably successful in removing the Chromate from industrial effluents and natural lake samples as detailed in TABLE No:2

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