

**ADSORPTION POTENTIALITIES OF BIO-SORBENTS DERIVED FROM *PROSOPIS CINERARIA*  
AND *HIBISCUS ROSA-SINENSIS* IN THE REMOVAL OF METHYL ORANGE DYE FROM  
POLLUTED WATERS**

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**ABSTRACT:** Leaves, stems and their ashes of *Prosopis cineraria* and *Hibiscus rosa-sinensis* have been explored for their surface sorption abilities towards Methyl Orange Dye using simulated waters. Various physicochemical parameters such as pH, time of equilibration and sorbent concentrations are optimized for evoking the sorption potentialities of the plant materials for the maximum extraction of the Methyl Orange Dye from waters. The surface sorption nature is found to be pH sensitive and % of removal is maximum near pH: 3. % removal of the Dye is more with ashes than respective bio-materials. Co-anions, in fivefold excess, are found to be interfering in the order: trivalent anion > divalent > monovalent while co-cations have shown relatively less interference on the extraction of the Dye at optimum conditions of extraction. The adoptability of the methodologies developed is tested with some real industrial effluents.

**Key words:** Methyl Orange Dye, Pollution Control, Bio-sorbents, *Prosopis cineraria*, *Hibiscus rosa-sinensis*, Applications

## INTRODUCTION

The effluents from dye-based industries contain synthetic dyes which are chemically and photologically stable and are not affected by heat and oxidizing agent (Leechart, et. al., 2009; Bhatnagar, et. al., 2005; Chung, et. al., 1981). If the dye residues in the wastewaters of industries are not removed before disposal, these dyes enter into nearby water bodies. As they are less prone for degradation, these synthetic dyes get accumulated in water bodies with the progress of time and turn to be potential threat to aquatic life as most of these dyes have azo groups with aromatic structures which are toxic or mutagenic for life (Gao, et. al., 2010; Bhatnagar and Jain, 2005; Chung, et. al., 1981). Further, the presence of the colored dyes in natural bodies curtail the sunlight to reach to the aquatic life and stops or deactivates some of the vital photo-sensitive chemical reactions necessary to aquatic life. This results in the loss balance in ecosystems in water bodies (Gottlieb, et. al., 2003). Thus the removal synthetic dyes from waste waters assume importance.

Some researchers developed procedures based on Electro-kinetic coagulation, ion-exchange, membrane filtration, electrochemical oxidation and photo-catalytic degradation process (Laszlo, 1996; Gemea, et. al., 2003; Grimau and Gutierrez, 2006; Hachem, et. al., 2001; Cisneros, et. al., 2002; Gukpta Suhas, 2009; Srivastava, et. al., 2006) but these methods are costly and are not application for large scale treatments.

Increasing research interest is being envisaged during the recent past, in evoking the sorption nature of Biomasses and bio-wastes of flora or fauna origin either in their native form or chemically modified form in removing the dyes in waste waters [Namasivayam, et. al., 1996; 1998; Gupta, et. al., 2004; 2005; Mittal, et. al., 2005; McKay, et. al., 1986; Ramakrishna and Sharma, 2003; Bhattacharya and Sharma, 2003; 2005; Kargi and Ozmihc, 2004; Dogan, et. al., 2004; Gong, et. al., 2005; Mahir, et. al., 2005; Armagan, 2004; Kannana and Sundaram, 2001; Manju, et. al., 1998; Hameed and EI-Khaiary, 2008; Waranusantigual, et. al., 2003; Otero, et. al., 2003; Jadav and Vanjara, et. al., 2004; Bansal, et. al., 2009; Jain and Sikarwar, 2006; Mall et. al., 1996; Bailey, et. al., 1999; Demirbas, 2009; Garg, et. al., 2004; Shukla et. al., 2002).

These methods are proving to be potential alternatives to the classical and traditional methods of pollution prevention and are stimulating continuous and expanding research in this field. Our research group is thriving in this aspect of pollution research and some successful eco-friendly methodologies have been developed (Hanumantharao, et. al., 2012a & b; Krisna Veni and Ravindhranath, 2012 a & b; Divya Jyothi, et. al., 2012 a, b & c ; Suneetha and Ravindhranath, 2012; Subbarao, et. al., 2012; Anna Aruna Kumar and Ravindhranath, 2012) for extracting some polluting ions of interest. Methyl orange (MO) is widely used in laboratory analysis, textiles and other commercial products and it has toxic nature towards aquatic life. So, its removal from waste waters, assumes importance (Mittal, et. al., 2007; Chen, et. al., 2010). Mittal et al (2007) studied the removal and recovery of Methyl Orange from wastewaters using waste materials. Chen S et al (2010) probed the equilibrium and kinetic aspects of Methyl Orange adsorption on activated carbon derived from Phragmites australis. Ru Jiang et al (2012) studied the removal of Methyl Orange from aqueous solutions by Maghemite/Chitosan Nanocomposite Films. F. Mogaddasi et al (2010) studied the Kinetic and Thermodynamic aspects of the removal of Methyl Orange from aqueous solution by adsorption onto Camel Thorn Plant. These methods suffer from one or the other disadvantages and an eco-friendly, economical and effective method is still eluding the researchers.

The endeavor of the present work is to probe the sorption nature plant materials derived from of *Prosopis cineraria* and *Hibiscus rosa-sinensis* towards Methyl Orange Dye from polluted waters. The effect of different process conditions such as pH of the agitating equilibrium, time of equilibration, sorbent dosage and the presence of co-ions on the % removal of Methyl Orange Dye , have been investigated and the extractions conditions have been optimized. The methodologies developed are applied to industrial effluents

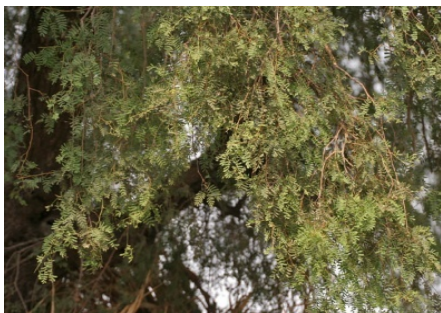
## MATERIALS AND METHODS

### Chemicals and Reagents

All chemicals used were of analytical grade. 10 ppm solution of Methyl Orange Dye was prepared by dissolving a requisite amount of A.R. grade Methyl Orange Dye in double distilled water and it was suitably diluted as per the need.

### ADSORBENTS

Various plant materials as bio-sorbents have been tried for the removal of Methyl Orange Dye from synthetically prepared polluted waters by optimizing various physicochemical parameters viz., pH, concentration of sorbent and time of equilibration. It has been observed that the sorbents derived from leaves and stems of *Prosopis cineraria* and *Hibiscus rosa-sinensis* plants have affinity towards the Methyl Orange Dye in the pH range 2-3. So, in the present investigation a thorough probe is made on these plant materials.



A: *Prosopis cineraria*



B: *Hibiscus rosa-sinensis*

Fig No. 1: Plants showing affinity towards Methyl Orange Dye

*Prosopis cineraria* are a species of flowering tree in the pea family, Fabaceae. It is native to arid portions of South Asia. It is a versatile species, providing fodder, fuel for timber and shade besides affecting the soil improvement and sand dune stabilization. It is commonly used in dry land agro forestry in India. It is also used in the preparation of some skin ointments. *Hibiscus rosa-sinensis* is an evergreen flowering shrub belongs to Malvaceae family and is grown throughout tropics and subtropics and is native to Asia. It is well accepted that the leaves and flowers of *Hibiscus rosa-sinensis* have hair growth promoting and anti-graying properties. In traditional medicine, the leaves of the plant are used in fatigue and skin disease. Fresh root juice of the plant is given for gonorrhoea and powder root for menorrhagia and further, it is reported that the plant parts have therapeutic using in curing epilepsy, leprosy, bronchial catarrh and diabetes (Gilani, et. al., 2005; Kasture, et. al., 2000; The Wealth of India- an Encyclopedia of CSIR, 1959). The leaves and stems of *Prosopis cineraria* and *Hibiscus rosa-sinensis* 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: < than 75 microns and activated at 105<sup>0</sup> C in an oven and then employed in this study. Further, these leaves or stem materials were burnt to ashes which were also used in this work.

### **ADSORPTION EXPERIMENT:**

Batch system of extraction procedure was adopted (Trivedy, 1995; Gerard Kiely, 1998; Metcalf and Eddy, 2003). Carefully weighted quantities of adsorbents were taken into previously washed 1 lit/500 ml stopper bottles containing 500 ml/250 ml of Methyl Orange Dye solution 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 the determination of Methyl Orange Dye using Spectrophotometric method. The Dye has  $\lambda_{max}$  at 464.9 nm and obey's Beers-Lamber's law at low concentrations. The O.D. measurements were made at the said  $\lambda_{max}$  using UV-Visible Spectrophotometer (Systronics make). The obtained O.D value for un-known solution was referred to standard graphs (drawn between O.D and concentration) prepared with known concentrations of Methyl Orange Dye by adopting method of Least Squares.

The sorption characteristics of the adsorbents were studied with respect to various physicochemical parameters. At a fixed sorbent concentration, the % removal of Methyl Orange Dye from simulated waters was studied with respect to time of equilibration at various pH values. The results obtained were presented in the Graph Nos. A: 1-8 and B: 1&2. To fix the minimum dosage needed for the maximum removal of the Methyl Orange Dye, for a particular sorbent at optimum pH and equilibration times, extraction studies were made by studying the % of extraction with respect to the sorbent dosage. The results obtained were presented in the Graph Nos. C: 1&2.

### **EFFECT OF OTHER CO-IONS (INTERFERING IONS)**

The interfering ions chosen for study were the common ions present in natural waters viz. Sulphate, Chloride, Nitrate, Phosphate, Carbonate, Calcium (II), Magnesium (II), Copper(II), Zinc(II) and Iron (II). The synthetic mixtures of Methyl Orange Dye and the co-ion ions were so made that the concentration of the foreign ion was maintained at five fold excess than the Dye concentrations as cited in the Table: 1. 500ml of these solutions were taken in stopper bottles and then correctly weighted optimum quantities of the promising adsorbents (as decided by the Graph Nos. A and B) were added. Optimum pH: 3 were adjusted with dil. HCl or dil. NaOH using pH meter. The samples were shaken in shaking machines for desired optimum periods and then small portions of the samples were taken out, filtered and analyzed for Methyl Orange Dye. % of extraction was calculated from the data obtained. The results were presented in the Table: 1.

### **APPLICATIONS OF THE DEVELOPED BIO-SORBENTS:**

The adoptability of the methodologies developed with the new bio-sorbents derived from *Prosopis cineraria* and *Hibiscus rosa-sinensis* plants in this work for removing Methyl Orange Dye from waste waters, was tried with some real sewage/effluent samples of some industries.

**Table No.:1: Effect of interfering Ions on the Extractability of Methyl Orange Dye with different Bio-sorbents**

Adsorbent and its concentration	Maximum Extractability at optimum conditions	% of Extractability of Methyl Orange Dye in presence of fivefold excess of (50 ppm) interfering ions at optimum conditions: Conc. of Methyl Orange Dye: 10.0 ppm									
		SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	Cl <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Ca <sup>2+</sup>	Cu <sup>2+</sup>	Fe <sup>2+</sup>	Zn <sup>2+</sup>	Mg <sup>2+</sup>
Leaves powder of <i>Prosopis cineraria</i>	89.0%; pH: 3; 60 minutes; sorbent conc.: 0.75 g/500 ml	20.0	12.0	62.0	21.5	63.0	64.0	52.0	59.0	62.0	59.0
Leaves Ash of <i>Prosopis cineraria</i>	95.3%; pH:3;45 min; Sorbent conc.:0.5g/500 ml	19.5	14.5	61.0	23.0	64.0	66.5	54.0	62.4	63.0	61.0
Stem powders of <i>Prosopis cineraria</i>	90.5%; pH:8; 60 minutes; Sorbent conc.:0.5 g/500 ml	21.0	13.0	69.0	25.0	62.0	67.2	56.0	61.0	58.0	60.0
Stems ash of <i>Prosopis cineraria</i>	96.7%;pH:3, 45 minutes; Sorbent conc.: 0.25 g/500 ml	23.0	16.7	70.0	26.0	63.0	63.5	58.4	63.5	59.0	61.0
Leaves powder of <i>Hibiscus rosa-sinensis</i>	85.0%; pH:3; 60 minutes; Sorbent conc.:0.5 g/500 ml	18.0	10.0	71.0	20.0	59.5	60.0	60.0	58.0	55.0	59.0
Leaves Ash of <i>Hibiscus rosa-sinensis</i>	88.7%; pH:3; 45 minutes; 0.25 gm/500 ml	24.5	17.0	65.0	23.0	60.1	61.0	62.3	60.5	57.0	62.5
Stem powders of <i>Hibiscus rosa-sinensis</i>	87.0%; pH:8; 45 minutes; Sorbent Conc.: 0.5 g/500 ml	22.0	18.0	68.0	25.0	58.0	62.0	61.5	60.0	58.0	60.5
Stem ash of <i>Hibiscus rosa-sinensis</i>	92.0%; pH:3; 30 minutes; Sorbent Conc.: 0.25 g/500 ml	23.0	15.0	69.5	20.5	59.0	65.0	64.5	63.5	60.0	62.0

For this purpose, samples were collected from effluents of some Dyeing industries at Hyderabad and Bombay and the samples were analyzed for actual amounts of Methyl Orange Dye and samples were fed with known amounts of Methyl Orange Dye if needed. Then these samples were subjected to extraction for the Dye adopting the methodologies developed in this work at optimum conditions of extraction as given in the Table 2. The results obtained were presented in the Table 2.

**Table No.2: % of Extractability of methyl orange dye from different industrial effluents with bio-sorbents developed in this work**

Bio-Sorbent	% of Extractability of Methyl Orange Dye				
	Sample 1: Fed with 5.0 ppm of Methyl Orange Dye	Sample 2 Fed with 7.5 ppm of Methyl Orange Dye	Sample 3 Fed with 10.0 ppm of Methyl Orange Dye	Sample 4 Fed with 12.5 ppm of Methyl Orange Dye	Sample 5 Fed with 15.0 ppm of Methyl Orange Dye
Leaves powders of <i>Prosopis cineraria</i> :at pH: 3; Equilibration time: 60 minutes; sorbent con.: 0.75 g/500 ml	60.5	61.0	55.0	54.0	50.0
Leaves ashes <i>Prosopis cineraria</i> : at pH: 3; Equilibration time: 45 min; Sorbent conc.:0.5g/500 ml	62.0	63.5	61.0	57.0	53.0
Stem powders of <i>Prosopis cineraria</i> :at pH:3; Equilibration time: 60 minutes; Sorbent concentration: 0.5 g/500 ml	59.0	63.0	60.0	58.0	56.0
Stems ash of <i>Prosopis cineraria</i> :at pH:3; Equilibration time:45 minutes; Sorbent concentration: 0.25 gm/500 ml	63.0	64.0	64.5	60.5	60.0
Leaves powders of <i>Hibiscus rosa-sinensis</i> : at pH:3; Equilibration time: 60 minutes; Sorbent concentration: 0.5 g/500 ml	55.0	56.9	60.2	63.0	61.0
Leaves ash of <i>Hibiscus rosa-sinensis</i> at pH:3; Equilibration time: 45 minutes; Sorbent concentration: 0.25 g/500 ml	57.0	59.0	65.0	65.0	63.0
Stems powder of <i>Hibiscus rosa-sinensis</i> :at pH:3; Equilibration time: 45 minutes; Sorbent concentration: 0.5 g/500 ml	63.0	61.0	59.0	64.7	59.0
Stems ash of <i>Hibiscus rosa-sinensis</i> at pH:3; Equilibration time: 30 minutes; Sorbent concentration: 0.25 g/500 ml	65.0	63.1	62.0	67.0	63.0

## RESULTS AND DISCUSSIONS

The data obtained is presented in the Graph No. A: 1-8; B: 1&2; C: 1&2.

The following *observations are significant*:

1. % of removal of Methyl Orange Dye is found to be increasing 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 (vide Graph Nos.: A: 1-8). At this steady state, rate of adsorption of the dye onto the surface of the adsorbent is equal to the rate of desorption.

With the plant materials of *Prosopis cineraria*, % of removal of Methyl Orange Dye at pH:3 has been found to be 49.0% at 15min, 67.6% at 30 min, 83.4% at 45 min, 89.0% at 60 min or above for leaves powders (Graph No. A: 1); 56.0 at 15 min, 80.3% at 30 min, 85.3% at 45 min or above for leaves ashes (vide Graph No. A: 2); 54.0% at 15 min, 69.7% at 30 min and 85.6% at 45min, 90.5% at 60 min or above for stems powder (vide Graph No. A: 3); and 56.7% at 15 min, 73.2% at 30 min, 96.7% at 45 min or above for the ashes of stems (vide Graph No. A: 4).

With the bio-materials of *Hibiscus rosa-sinensis*, the % of extraction of the Dye at pH:3 has been found to be 26.9 % at 15min, 41.0 % at 30 min, 65.0% at 45 min, 85.0% at 60 min or above for leaves powders (vide Graph No. A: 5); 35.9% at 15 min, 56.3 at 30 min, 88.7% at 45 min or above (vide Graph No. A: 6) for leaves ashes; 31.2% at 15 min, 60.0% at 30 min and 87.0% at 45min or above for stems powder (vide Graph No: 7); and 56.8% at 15 min, 92.0% at 30 min or above for the ashes of stems (vide Graph No.8).

2. **Effect of pH:** The % of extraction is found to be pH sensitive. The adsorption of the dye onto the surface of the adsorbents is more in the pH range 2 to 3 and above and below this pH range, the adsorption is progressively decreasing (Vide Graph No. B: 1 and 2).

As for example, with the leaves powder of *Prosopis cineraria*, the maximum extractability, has been found to be 15.2% at pH: 0 (1.0 N HCl); 22.3% at pH:1; 79.5% at pH:2; 89.0% at pH:3; 56.0% at pH:4; 43.4% at pH:5; 32.0% at pH:6; 28.5% at pH:7 and 24.5% at pH:8 while with the ashes of leaves of *Prosopis cineraria*, the maximum % removal of the Dye has been found to be: 16.0% at pH:0 (1.0 N HCl), 32.0% at pH:1; 82.5% at pH:2; 95.3% at pH:3; 60.0% at pH:4; 48.0% at pH:5; 38.0% at pH:6; 31.0% at pH:7 and 26.0% at pH:8 (vide Graph No.B:1). With the stems powder of *Prosopis cineraria*, the % of extraction has been found to be 17.0, 27.7, 84.1, 90.5, 50.1, 42.0, 36.0, 32.0 and 27.0 at pHs: 0(1.0 N HCl), 1, 2, 3, 4, 5, 6, 7 and 8 respectively; with the stems ashes, the % of extraction has been found to be 15.3, 34.6, 88.5, 96.7, 56.7, 45.5, 37.2, 34.0 and 28.0 respectively for the same sequence of pHs (vide Graph No: B:1).

Similarly with the plant materials of *Hibiscus rosa-sinensis*, the maximum % removal at pH: 0 (1.0 N HCl), 1, 2, 3, 4, 5, 6, 7, and 8 has been found to be respectively : 12.5%, 18.6%, 72.0%, 85.0%, 34.9%, 17.8%, 20.0%, 15.4% and 9.2% for leaves powder; 13.5%, 19.5%, 78.5%, 88.7%, 40.3%, 32.3%, 25.0%, 19.0% and 11.5 for leaves ash; 11.0%, 19.0%, 74.3%, 87.0%, 36.0%, 29.7%, 22.0%, 16.5% and 10.1% for stems powder; 12.9%, 30.5%, 82.5%, 92.0%, 50.0%, 35.0%, 25.0%, 18.5% and 12.0% for stems ash (Vide Graph No.B:2)

3. **The optimum time of agitation time** is found to be less for ashes than with the respective raw plant materials. For *Prosopis cineraria* leaves powder, the optimum time is found to be 60 min while for their ashes it is 45 min only. With the stems powder of *Prosopis cineraria* plant, the optimum time is found to be 45 min but 30 min is sufficient with their ashes as sorbents. With *Hibiscus rosa-sinensis* leaves powder as adsorbent, the optimum agitation time has been found to be 60 min but with their ashes, it has been reduced to 45 min; with stems powder of the same plant, optimum equilibration is found to be 45 min while 30 min of agitation is enough with ashes stems (vide Graph No .A:1-8).

#### 4. Adsorbent Dosage:

When percentage removal is studied with respect to adsorbent dosage at fixed optimum pH: 3 and at optimum equilibration times, the graphs increase up to certain dosage and from then onwards plateaus are obtained (Vide Graph No. C: 1 &2). The optimum sorbent dosage has been to be less for ashes than the raw plant materials.

With the sorbent pertaining to Prosopis cineraria plant, the optimum adsorbent concentration has been found to be: 0.75 gm/500ml for leaves and 0.5 gm/500 for their ashes; 0.5 gm/500ml for stem powders and 0.25 gm/500ml for their ashes (vide Graph No.C:1).

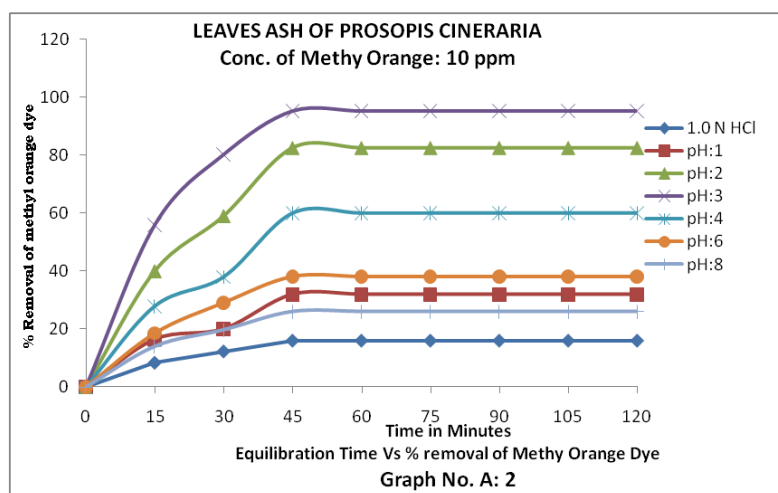
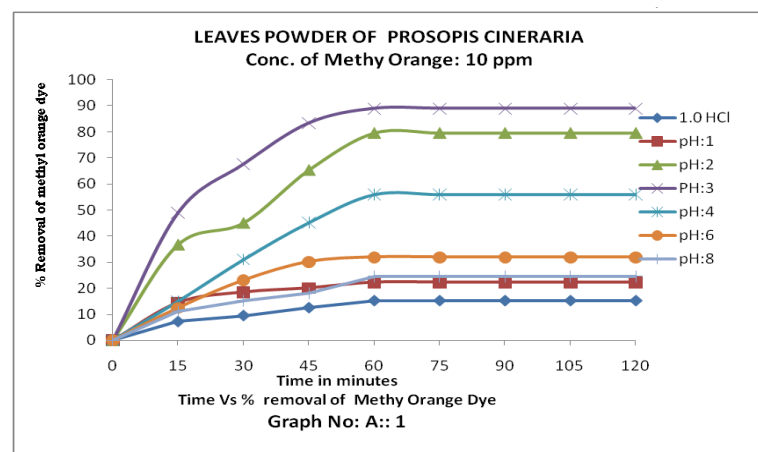
In the case of Hibiscus rosa-sinensis plant, the optimum sobent dosage has been found to be: 0.5 gm/500ml for leaves or stems powder while 0.25 gm/500ml for their ashes. (vide Graph No.: C: 2).

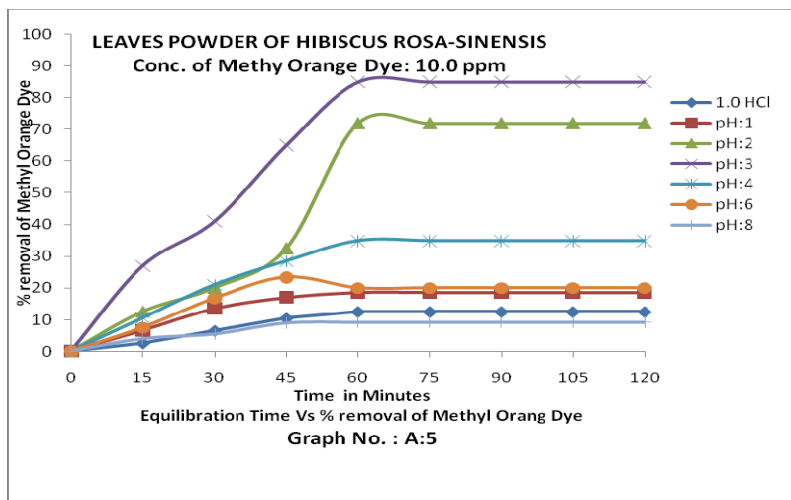
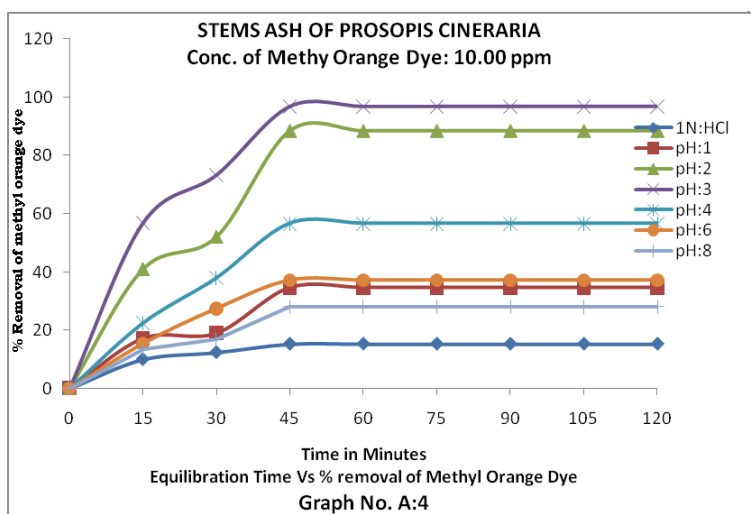
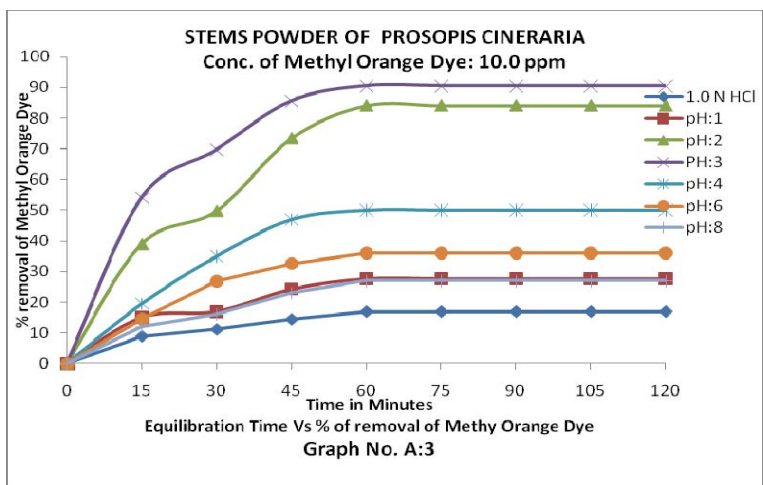
#### 5. Interfering Ions:

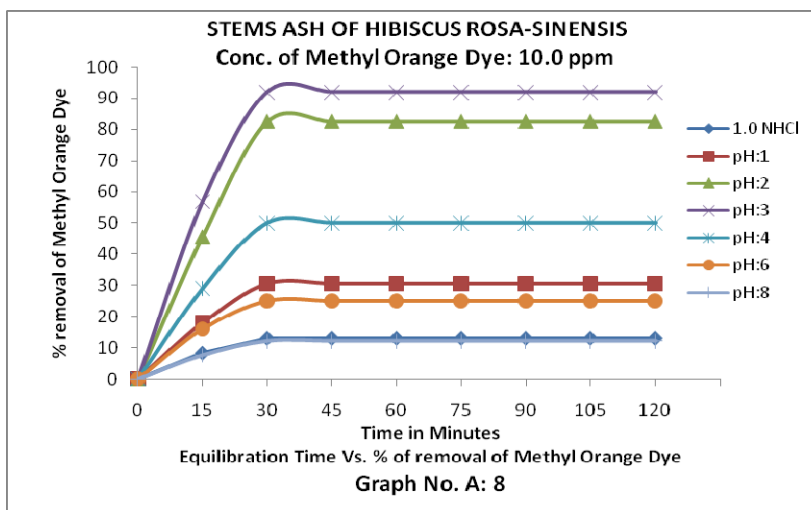
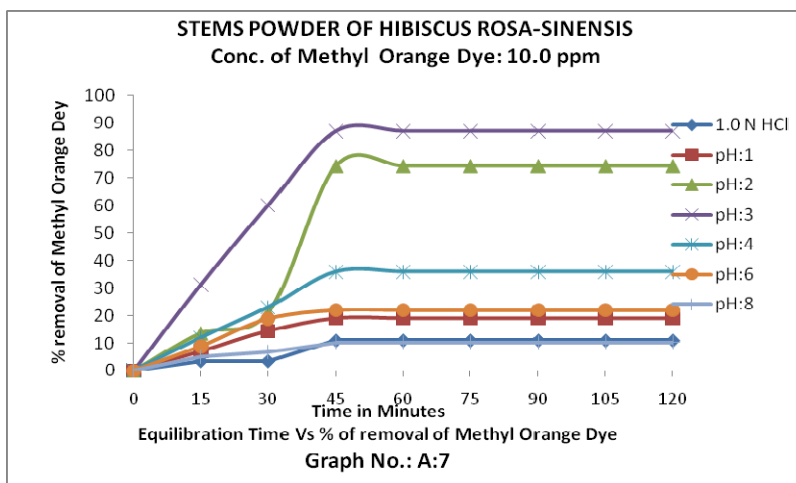
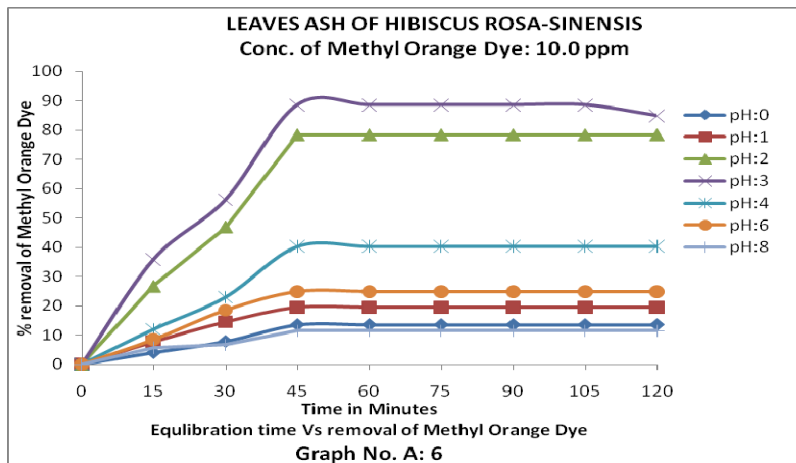
The effect of the presence of fivefold excess of co-ions on the % removal of the Methyl Orange Dye from simulated waters, has been studied and the results have be presented in the Table No.1. Co-anions are found to be interfering in the order: trivalent anion>divalent > monovalent while co-cations have shown relatively less interference on the extraction of the Dye at optimum conditions of extraction

In the case of anions, the % removal is found to be only : 18.0% to 24.5% with  $\text{SO}_4^{2-}$  as co-ion; 10.0 to 18.0% with Phosphate; and 20.0 to 26.0% with  $\text{CO}_3^{2-}$ ; 61.0% to 71.0% with  $\text{Cl}^-$  and 58.0 to 64.0% with  $\text{NO}_3^-$  (Vide Table 1: Column Nos. 3 to 7).

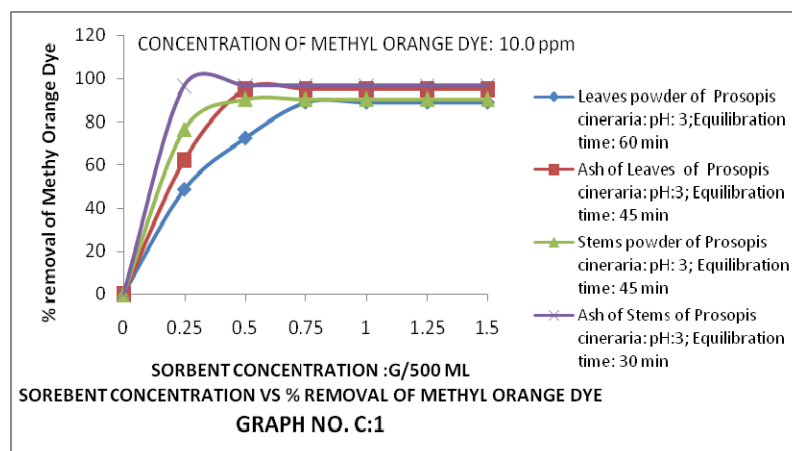
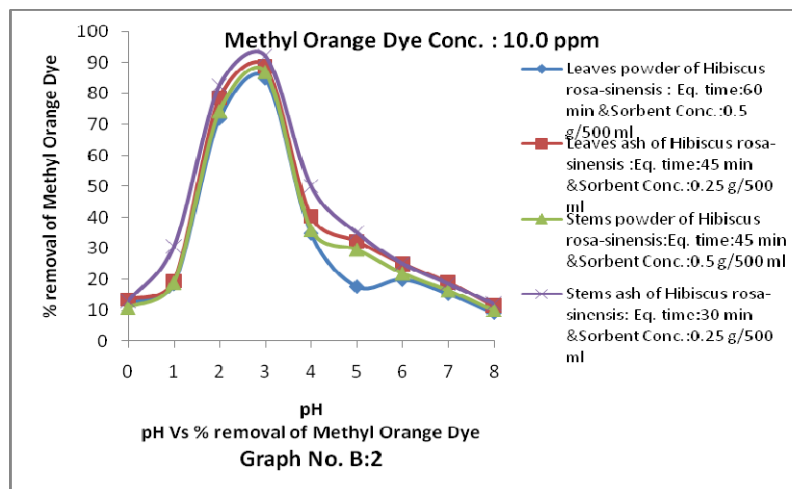
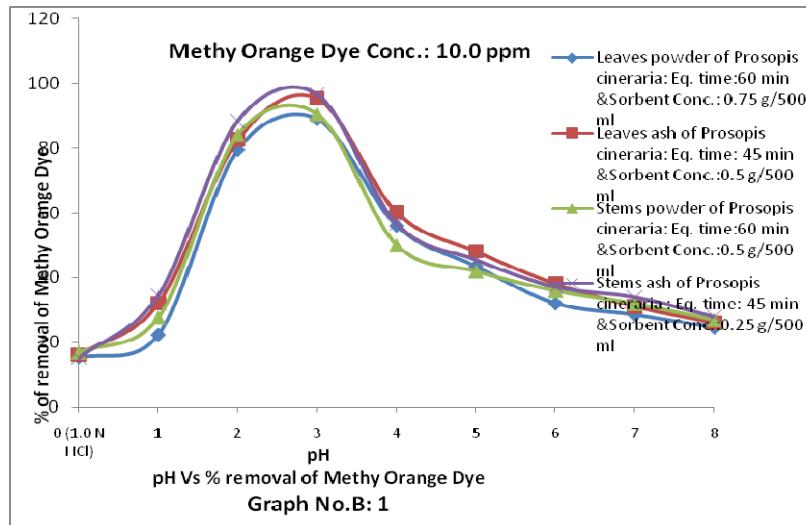
In the case of fivefold excess of co-caions, the extraction has been found to be: to 60.0 to 67.2% with  $\text{Ca}^{2+}$  as co-ion; 52.0 to 64.5% with  $\text{Cu}^{2+}$ ; 58.0 to 63.5% with  $\text{Fe}^{2+}$ ; 55.0 to 63.0% with  $\text{Zn}^{2+}$  and 59.0 to 62.5% with  $\text{Mg}^{2+}$  (vide Table No.1: Column Nos. 8 to -12)

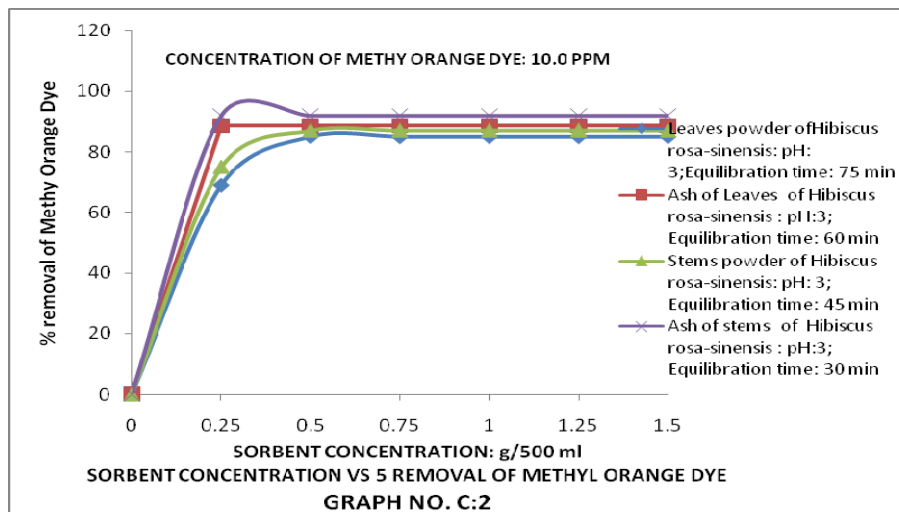










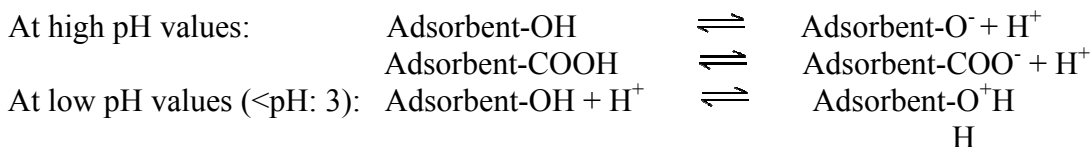


## DISCUSSIONS

For a thorough understanding of the sorption mechanism of these bio-adsorbents towards the Methyl Orange Dye, surface morphological studies using such modern instruments like X-ray Photo Electron Spectroscopy (XPS), Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscope (SEM) and Energy Dispersive Spectrum (EDS) in addition to the conventional analytical procedures before and after the sorption of the anionic dye onto the surface of the sorbent, are needed. It is beyond the aims of this work.

However, the observations may be accounted as follows:

- The sorbents derived from plant materials may have some functional groups like -OH/COOH and their dissociation is pH dependent. This imparts weak anion exchange ability at low pH: < 3 values and weak cation exchange ability at high pH values as per the equilibrations:



The acid dissociation constant of Methyl Orange Dye is: pK: 3.7 and the dye will dissociation and thereby yielding to anionic species in the transition pH range 3.1 to 4.4 and at this pH range, the dye will be changing from quononoid form to benenoid form. If the Dye is in anionic form and surface is positively charged, then adsorption of the Dye is more. The Dye will be anionic form only above 3.1 as the pH transition range is: 3.1 to 4.4 while the protination of the sorbent occurs at low pH values less than 3. So, the Dye shows more sorption near pH: 3. If the pH is more than 3, protination is less favored and further, Hydroxide ions compete with the anion of Dye for the ion-exchange sites of the sorbents and thereby, adsorption is less. If the pH is decreased below 3, protination of the sorbent surface occur but the *Dye is in un-dissociated form* and it loses its affinity towards the sorbent surface via ion-exchange. However, the van der Waals interactions and Hydrogen bonding formations between surface and dye may prevail but these forces will be nullified due the presence of aquated Hydronium ions in the contacting solution of the sorbent surface.

The net result is that the Dye is showing affinity towards the sorbents around pH: 3. Increasing or decreasing of the pH (other than optimum pH: 3), of the agitating solution, results in the decrease in sorption. The rate of adsorption is found to be more initially but decreases with time and reaches steady state after certain time. This is due to the fact that initially many active sites are available for the sorption process to occur and they are progressively used up with time and hence, rate of adsorption is decreased. But after a certain time, there will not be active sites on the sorbent surface for the adsorption process to take place i.e. a saturation stage is reached and at this stage, there will not be further adsorption. Ashes are the oxides of some heavy metals containing large amounts of silica. The ashes, contains '-OH' groups and '-O-' and observed surface sensitivity may be accounted in the same lines as described in the case of raw leaves or stem powders. In fact, in the literature it is reported that the silica possesses cation exchanging nature (Parks, 1965; 1967; Ravindhranath and Janardhan, 1987) and this supports the proposed logic for the observed behavior. The observed data pertaining to the effect of co-ions on the extraction the Dye confirms this concept. The trivalent and bivalent anions having more negative charge than monovalent anions, inhibit the adsorption of anionic Methyl Orange Dye on to the surface of the sorbents while cations have been found to less effect the adsorption of the Dye because at pH: 3, the surface of the of sorbent is protonated and the prevailing positive charge on the surface repels the cations.

## APPLICATIONS

The bio-methodologies developed have been applied for samples collected from the sewage/effluents of some Dyeing industries which are fed with varying quantities of the Methyl Orange Dye. **The results have been presented in the Table No: 2.** It can be inferred from the data that with sorbents developed in this work, 50-67% Methyl Orange Dye can be removed from the waste waters at optimum conditions of extraction as cited in the Table No. 2.

## CONCLUSIONS

1. Plant materials pertaining to *Prosopis cineraria* and *Hibiscus rosa-sinensis* plants have been probed for their sorption potentialities towards Methyl Orange Dye from polluted waters.
2. Various physicochemical conditions such as pH, sorbent dosage and time of equilibration have been optimized for the maximum extraction of Methyl Orange Dye.
3. % removal of the dye is found to pH sensitive and the sorbents have shown greater affinity towards the Methyl Orange Dye near pH: 3.
4. % removal is more with ashes than with their respective raw bio-materials.
5. Co-anions, in fivefold excess, are found to be interfering in the order: trivalent anion > divalent > monovalent while co-cations have shown relatively less interference on the extraction of the Dye at optimum conditions of extraction
6. The adoptability of the methodologies developed is tested with some real industrial effluents.

**ACKNOWLEDGEMENT:** The authors thank UGC for financial aid.

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