Extraction of methyl orange dye from polluted waters using bio-sorbents derived from *Thespesia populnea and Pongamia pinnata* plants

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ABSTRACT

The sorption abilities of thermally activated powders of leaves, stems and their ashes of Thespesia populnea and Pongamia pinnata plants have been probed for the extraction of Methyl Orange Dye from polluted waters. Various Physicochemical parameters such as pH, time of equilibration and sorbent dosage, have been optimized for the maximum removal of the Dye. The Dye sorption has been found to be sensitive to pH and high affinity of the sorbents towards the Dye has been found around pH: 3. Ashes have been found to be more effective than raw bio-materials. Fivefold excess of common trivalent and divalent anions ions present in natural waters, markedly affected the % of removal than monovalent ions. Cation like Ca^{2+}, Mg^2 , Cu^{2+} Fe^{2+} and Zn^{2+} have interfered to some extent. The methodologies developed have been applied to industrial effluents.

Key words: Methyl Orange Dye, Pollution Control, Bio-sorbents, *Thespesia populnea, Pongamia pinnata*, Applications

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INTRODUCTION

Removal of synthetic dyes from wastewaters is one of the major concerns for the researchers working in Pollution control methods. The synthetic dyes are extensively used in textile and paper industry. The effluents from these industries naturally have appreciable quantities of the dyes. These synthetic dyes, unlike natural dyes, are non-degradable to micro-organisms with time and as a consequence of this, the presence of synthetic dyes is increasing in the nearby water-bodies of industries. Most of the synthetic dyes have active aromatic azo that are dissociated to toxic compounds harmful to organisms [1-3]. Moreover, the residual amounts of the dyes in water bodies impart color to the waters and the color of the waters, blocks the Sun radiation to reach the aquatic plantation and organisms and thereby affecting the photosynthetic and microbiological activity [4] and as a consequence of which, the eco-systems in the water bodies are disturbed.

Literature survey indicates that growing interest is being envisaged in developing the methodologies to remove or control Dyes from polluted waters. Various methods based on Electro-kinetic coagulation, ion-exchange, membrane filtration, electrochemical oxidation and photo-catalytic degradation process have been tried [5-9] but these methods suffer from high cost and are not viable in developing countries like India and are less encouraging for adoption for treating waters in large scale. Coagulation methods have sludge disposal problem [10] while Ion-exchange and Membrane separation methods are costly though effective [11]. The conventional biological decomposition methods are not effective [9].

In this context 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 and it is stimulating the continuous and expanding research in this field [12-38].

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Methyl orange (MO) is a commonly used monoazo dye in laboratory assays, textiles and other commercial products and has to be removed from water due to its toxicity [39, 40]. Mittal et al [39] studied the removal and recovery of Methyl Orange from wastewaters using waste materials.

Chen S et al [40] probed the equilibrium and kinetic aspects of Methyl Orange adsorption on activated carbon derived from *Phragmites australis. Ru Jiang [41] studied the removal of Methyl Orange from aqueous solutions by Maghemite/Chitosan Nanocomposite Films. F. Mogaddasi et al [42] studied the Kinetic and Thermodynamic aspects of the removal of Methyl Orange from aqueous solution by adsorption onto Camel Thorn Plant..*

In the present work, the sorption abilities of bio-adsorbents derived from some plants have been explored towards the extraction of Methyl Orange Dye from polluted waters by optimizing the physicochemical parameters such as pH, time of equilibration and sorbent concentration. Further, the procedures developed have been applied to samples from industrial effluents for finding their adoptability.

MATERIALS AND METHODS

(A) CHEMICALS: All chemicals used were of analytical grade.
Stock solution of Methyl Orange Dye: 10 ppm of Methyl Orange solution was prepared by dissolving a requisite amount of A.R. grade Methyl Orange Dye in double distilled water**.** It was suitably diluted as per the need.

(B) ADSORBENTS:
While we are making some pilot studies in exploring the sorption characteristics of some plant materials towards Methyl Orange Dye, a strong affinity between the Dye and plant materials of **Thespesia populnea and Pongamia pinnata has** been noticed. In the present study, surface sorption nature of the bio-materials of these plants has been explored.

A: Thespesia populnea   *B: Pongamia pinnata*

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

Thespesia populnea, commonly known as the **Portia Tree** is a small tree or shrub and it belongs to mallow family, Malvaceae. It grows in the wide range of   soil types that may be present in coastal environments, including soils derived from quartz, limestone and basalt and favors neutral soils (pH of 6-7.4) [43]. The color of heartwood of the Portia Tree is dark reddish brown to chocolate brown and is used in woodworks. The plant wood has religious sanctity and sculptures made with it are being preached traditionally.

Pongamia pinnata belongs to pea family, Fabaceae, native in tropical and temperate Asia and it grows to about 15–25 meters in height. The tree is well suited to intense heat and sunlight and its dense network of lateral roots and its thick and long taproot make it drought-tolerant. The dense shade it provides slows the evaporation of surface water and its root nodules promote nitrogen fixation. The plant is also used in the preparation for diesel for generators.

The leaves and stems of **Thespesia populnea and Pongamia pinnata** 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° C in an oven and then employed in this study. Further, these leaves or stem materials were burnt to ashes and these ashes were also used in this work.

 (C)ADSORPTION EXPERIMENT:
Batch system of extraction procedure was adopted [44-46]. 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

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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 λmax at 464.9 nm and obeys Beers-Lamber's law at low concentrations. The O.D. measurements were made at the said λmax 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 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.

(D) EFFECT OF OTHER 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 was 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.*

(E)APPLICATIONS OF THE DEVELOPED BIO-SORBENTS:
The adoptability of the methodologies developed with the new bio-sorbents derived from *Thespesia populnea and Pongamia pinnata* plants in this work for removing Methyl Orange Dye from waste waters , was tried with some real sewage/effluent samples of some industries. .

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.*

RESULTS AND DISCUSSION

The results obtained have been presented in the Graph No. A: 1-8; B: 1 &2; C: 1 & 2 and Table Nos. 1 and 2. *The following observations are significant:*

1. *Time of equilibration*: The agitation time has been found to have remarkable effect on the % of removal of the Dye. % removal is found to be increasing with the increase in the contact time at a fixed pH until a saturation state is reached and after such a time, the extractability remains constant (vide Graph Nos. A: 1-8).

The rate of adsorption is found to be more initially and with the increase of time, it decrease and after certain time, there has been found to be no further adsorption; in other words, steady state has been reached at which rate of adsorption is equal to the rate of desorption. As for example, in the case of plant materials of *Thespesia populnea, % of extraction of Methyl Orange Dye at pH:3 has been found to be 50.6% at 15min, 65.4% at 30 min , 85.3% at 45 min , 92.0% at 60 min or above for leaves powders (Graph No. A: 1); 60.4 at 15 min, 90.6 at 30 min, 96.7 at 45 min and above for leaves ashes (vide Graph No. A: 2); 75.8%% at 15 min, 83.6% at 30 min and 94.0% at 45min and above for stems powder (vide Graph No. A: 3); and 80.5% at 15 min, 98.9% at 30 min and above for the ashes of stems (vide Graph No. A: 4). Similarly with the bio-materials of Pongamia pinnata, the % of extraction of the Dye at pH:3 has been found to be 55.8 % at 15min, 57.2 % at 30 min , 68.7% at 45 min , 86.2% at 60 min or above for leaves powders(vide Graph No. A: 5); 38.1% at 15 min, 52.7 at 30 min, 91.0 at 45 min and above (vide Graph No. A:6) for leaves ashes; 74.9%% at 15 min, 93.1% at 30 min and 96.0% at 45min and above for stems powder (vide Graph No:7); and 88.4% at 15 min, 98.0% at 30 min and above for the ashes of stems (vide Graph No.8).*

2. *Effect of pH*: The sorbents of the present study have been found *to be pH sensitive. The sorption is more in the pH range 2 to 3 and above and below this pH range, the adsorption nature of the sorbents has been found to*
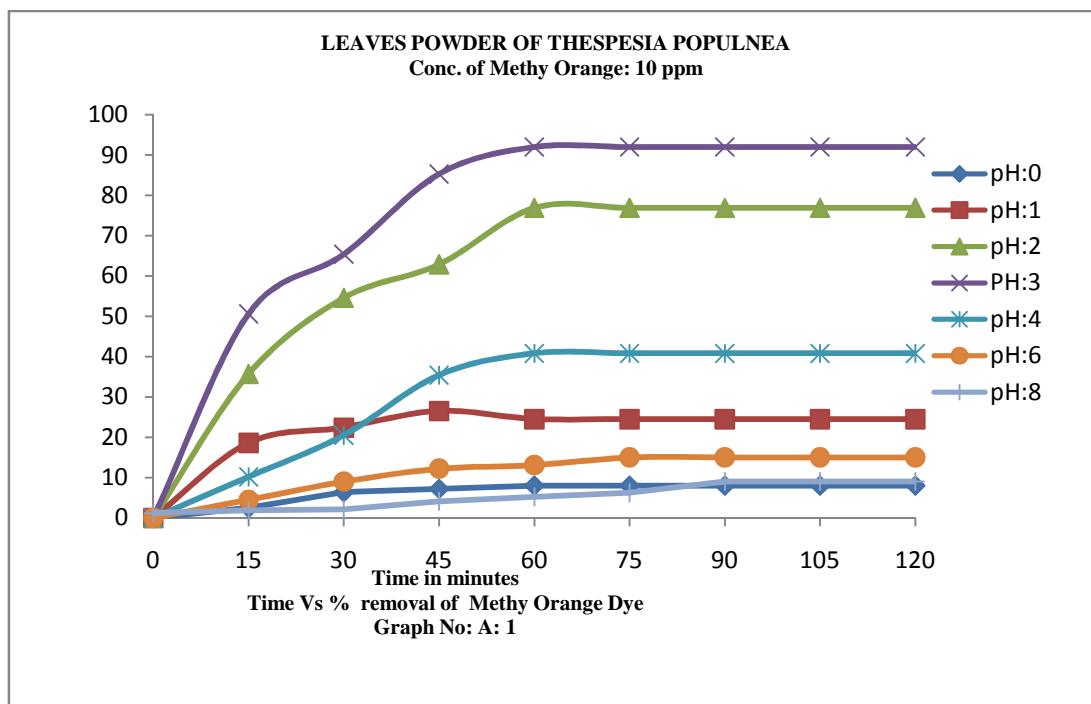
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*decreasing with respect the Methyl Orange Dye (Vide Graph No. B: 1 and 2). As for example, in the case of leaves powder of Thespesia populnea, the maximum possible removal of the Dye at optimum conditions of extraction, has been found to be 8% at pH: 0 (1.0 N HCl); 24.5% at pH:1;76.9% at pH:2; 92.0% at pH:3; 40.8.% at pH:4; 20.1% at pH:5; 13.1% at pH:6; 7.5% at pH:7 and 5.2% at pH:8 while with the ashes of leaves of Thespesia populnea, the maximum % removal of the Dye has been found to be: 12.0% at pH:0 (1.0 N HCl), 32.5% at pH:1; 85.6% at pH:2; 96.7% at pH:3; 55.0% at pH:4; 25.1% at pH:5;13.2% at pH:6; 10.2% at pH:7 and 3.2% at pH:8 (vide Graph No.B:1). With the stems powder of Thespesia populnea, the % of extraction has been found to be 9.0, 25.3, 78.9 94.0, 50.0, 30.0, 13.1, 9.0 and 2.0 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 14.0, 34.1, 78.2, 98.9, 62.0, 32.0, 6.7,4.7 and 3.1 respectively for the same sequence of pHs (vide Graph No: B:1).*
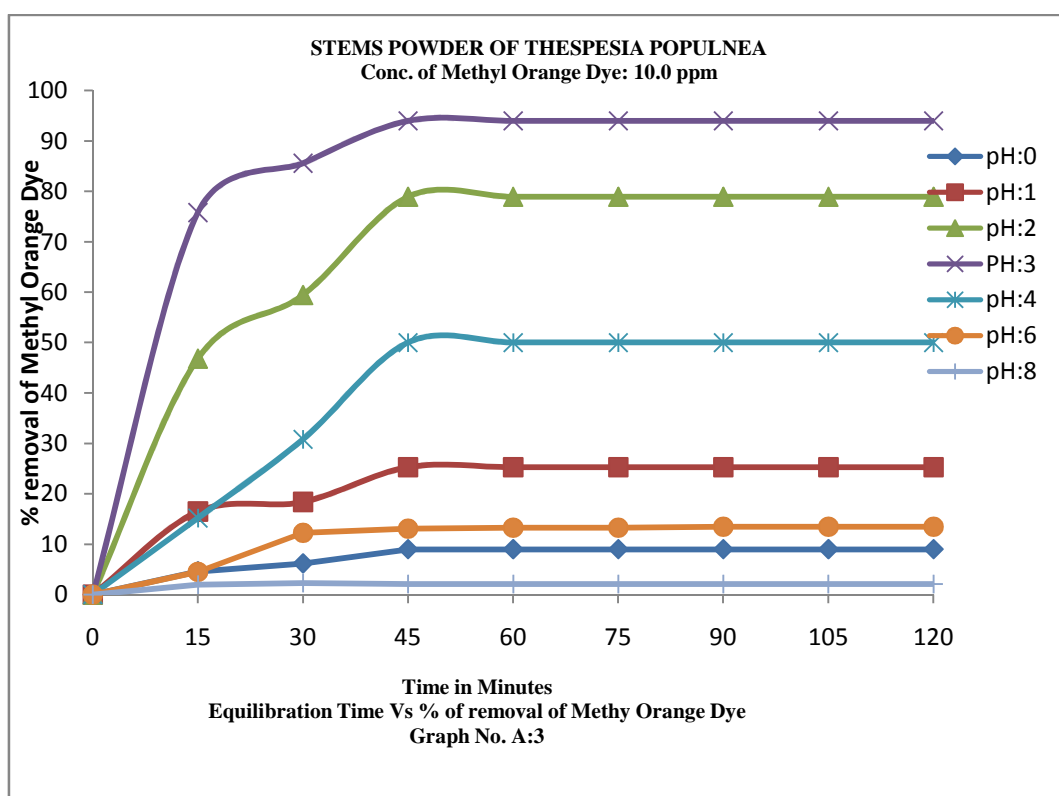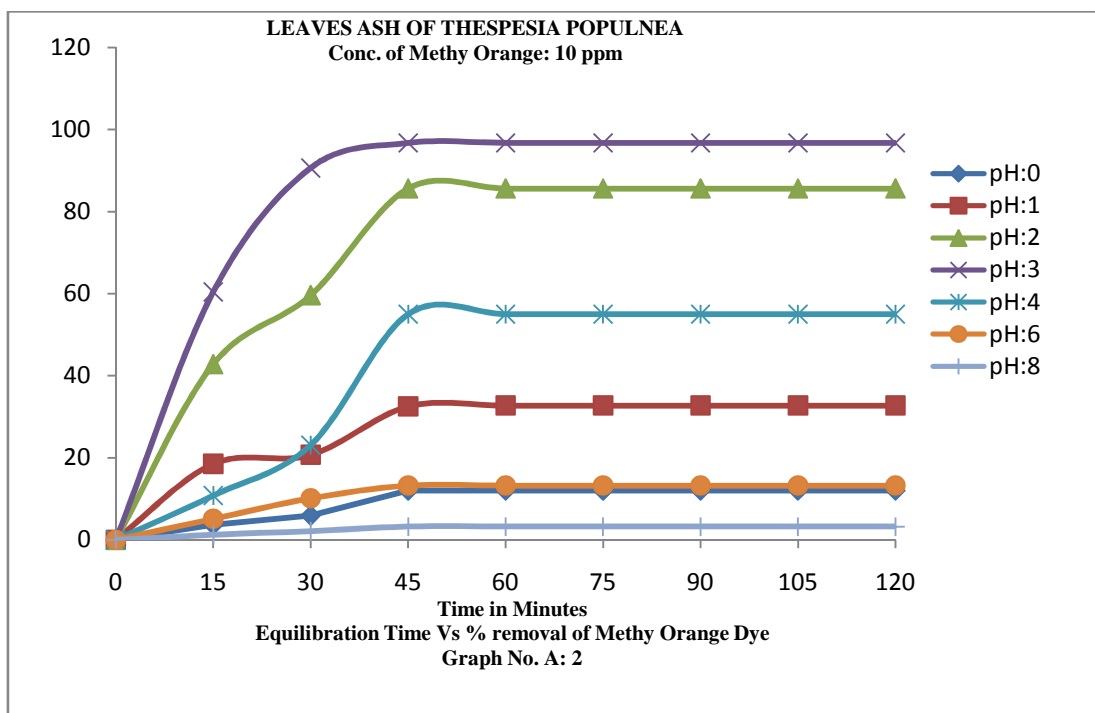
*Similarly with the plant materials of Pongamia pinnata, the maximum possible extraction at pH: 0 (1.0 N HCl), 1, 2, 3, 4, 5, 6, 7, and 8 has been found to **be respectively** : 11.9%, 20.6%, 73.9%, 86.2%, 34.5%, 21.0%, 11.0%, 9.0% and 7.8% for leaves powder; 12.5%, 25.0%, 55.3%, 91.0%, 40.8%, 30.3%, 12.1%,10.0% and 6.6 for leaves ash; 10.8%, 16.9%, 79.2%, 96.0%, 45.8%, 37.8%, 15.0%, 13.0%, and 6.8% for stems powder; 12.5%, 25.0%, 83.2%, 908.0%, 50.1%, 40.1%, 18.2%,14.1% and 6.9% for stems ash (Vide Graph No.B:2)*
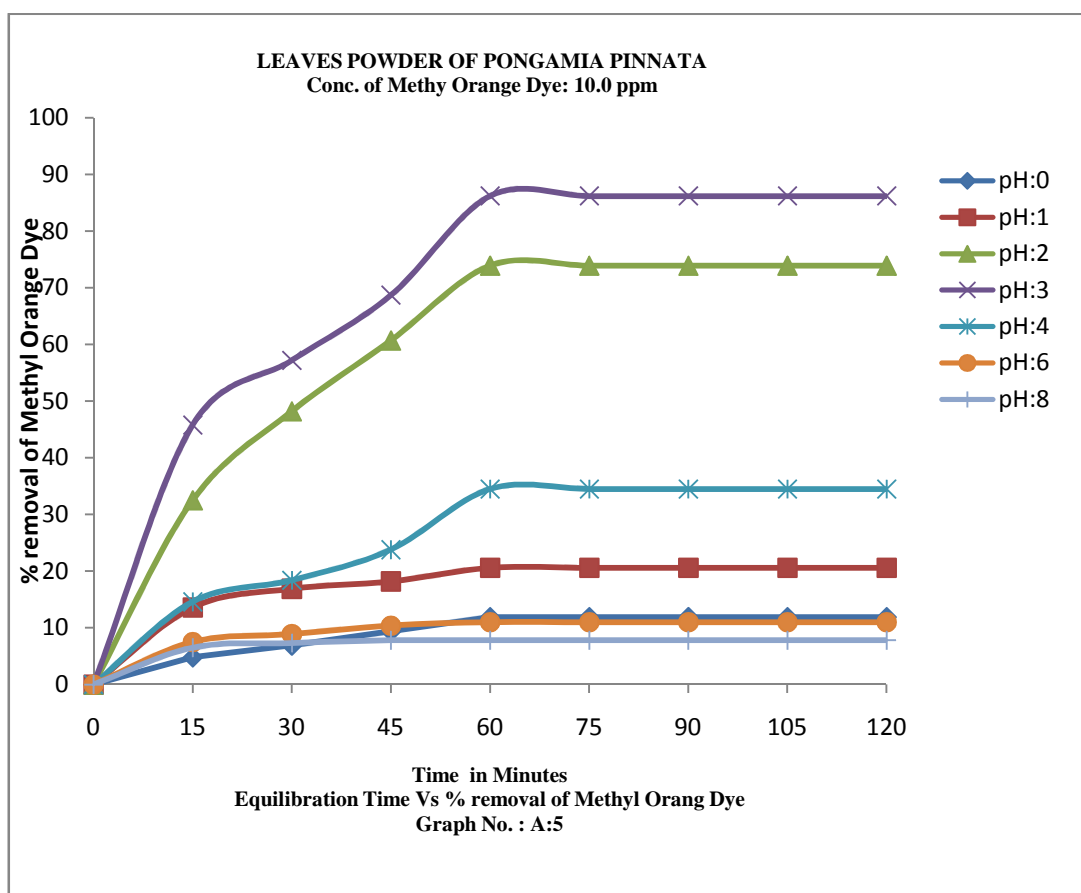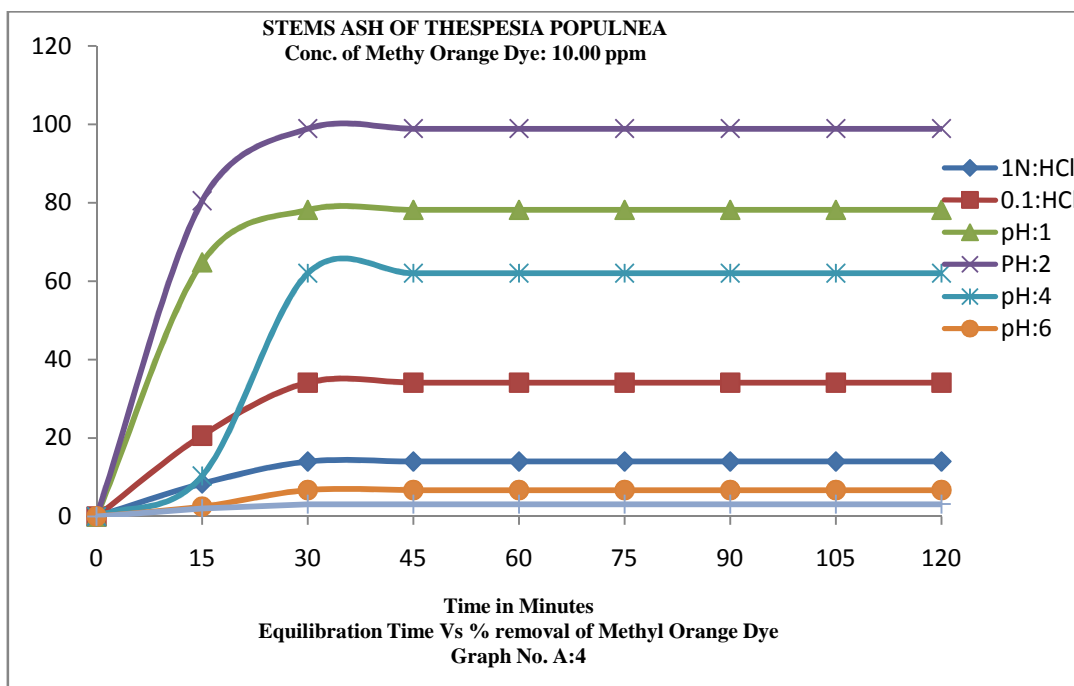
*3.**Optimum equilibration time:** The minimum time needed for the maximum extraction of the Dye under optimum conditions of extraction, is found to be less for ashes than with the respective raw plant materials. For both the plants, the optimum times have been found to be : 60 minutes for leaves powders while 45 minutes for their ashes; and 45 minutes for stems powders and 30 minutes for their ashes of the both plants (vide Graph No .A:1-8).*

*4.**Sorbent Concentration**:* The optimum sorbent dosage needed for the maximum extraction of the Methyl Orange Dye has been to *be less for ashes than the raw plant materials:* in the case of *Thespesia populnea*, 1.0 gm/500ml for *leaves powder while 0.75 gm/500 for their ashes; 0.5 gm/500ml for stem powders while 0.25 gm/500ml for their ashes (vide Graph No.C:1).* In the case of *Pongamia pinnata plant, the optimum sobent dosage has been found to be: 0.5 gm/500ml for leaves powder and 0.25 gm/500ml for their ashes; 0.5 gm/500 ml for stems powder and 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 extraction of the *Methyl Orange Dye* from *simulated waters,* has been probed and presented in the *Table No.1*. It can be inferred that bivalent anions like $CO_3^{2-}$and SO_4^{2-} and trivalent Phosphates interfered markedly while monovalent ions like Cl^- and NO_3^- interfered to a less extent. The common Cations namely, Ca^{2+}, Mg^{2+}, Fe^{2+}, Zn^{2+} and Cu^{2+} interfered to some extent.

LEAVES POWDER OF THESPESIA POPULNEA
Conc. of Methy Orange: 10 ppm

Time in minutes
Time Vs % removal of Methy Orange Dye
Graph No: A: 1

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LEAVES ASH OF THESPESIA POPULNEA
Conc. of Methy Orange: 10 ppm

Time in Minutes
Equilibration Time Vs % removal of Methy Orange Dye
Graph No. A: 2

STEMS POWDER OF THESPESIA POPULNEA
Conc. of Methyl Orange Dye: 10.0 ppm

Time in Minutes
Equilibration Time Vs % of removal of Methy Orange Dye
Graph No. A:3

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STEMS ASH OF THESPESIA POPULNEA
Conc. of Methy Orange Dye: 10.00 ppm

Time in Minutes
Equilibration Time Vs % removal of Methyl Orange Dye
Graph No. A:4

LEAVES POWDER OF PONGAMIA PINNATA
Conc. of Methy Orange Dye: 10.0 ppm

Time in Minutes
Equilibration Time Vs % removal of Methyl Orang Dye
Graph No. : A:5

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LEAVES ASH OF PONGAMIA PINNATA
Conc. of Methyl Orange Dye: 10.0 ppm

Equlibration time Vs removal of Methyl Orange Dye
Graph No. A: 6

STEMS POWDER OF PONGAMIA PINNATA
Conc. of Methyl Orange Dye: 10.0 ppm

Equilibration Time Vs % of removal of Methyl Orange Dye
Graph No.: A:7

STEMS ASH OF PONGAMIA PINNATA
Conc. of Methyl Orange Dye: 10.0 ppm

Equilibration Time Vs. % of removal of Methyl Orange Dye
Graph No. A: 8

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Methy Orange Dye Conc.: 10.0 ppm

Legend:
- Leaves powder of Thespesia Populnea :: Eq. time:60 min &Sorbent Conc.:1.0 g/500 ml
- Leaves ash of Thespesia Populnea: Eq. time:45 min &Sorbent Conc.:0.75 g/500 ml
- Stems powder of Thespesia Populnea: Eq. time:45 min &Sorbent Conc.:0.5 g/500 ml
- Stems ash of Thespesia Populnea: : Eq. time:30 min &Sorbent Conc.:0.25 g/500 ml

pH
pH Vs % removal of Methy Orange Dye
Graph No.B:1

Methyl Orange Dye Conc. : 10.0 ppm

Legend:
- Leaves powder of Pongamia Pinnata: Eq. time:60 min &Sorbent Conc.:0.5 g/500 ml
- Leaves ash of Pongamia Pinnata:Eq. time:45 min &Sorbent Conc.:0.25 g/500 ml
- Stems powder of Pongamia Pinnata:Eq. time:45 min &Sorbent Conc.:0.5 g/500 ml
- Stems ash of Pongamia Pinnata: Eq. time:30 min &Sorbent Conc.:0.25 g/500 ml

pH
pH Vs % removal of Methyl Orange Dye
Graph No. B:2

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CONCENTRATION OF METHYL ORANGE DYE: 10.0 ppm

Leaves powder of Thespesia populnea: pH: 3;Equilibration time: 60 min

Ash of Leaves of Thespesia populnea: pH:3; Equilibration time: 45 min

Stems powder of Thespesia populnea: pH: 3; Equilibration time: 45 min

Ash of Stems of Thespesia populnea: pH:3; Equilibration time: 30 min

SORBENT CONCENTRATION :G/500 ML
SOREBENT CONCENTRATION VS % REMOVAL OF METHYL ORANGE DYE
GRAPH NO. C:1

CONCENTRATION OF METHY ORANGE DYE: 10.0 PPM

Leaves powder of Pongamia pinnata: pH: 3;Equilibration time: 60 min

Ash of Leaves of Pongamia pinnata : pH:3; Equilibration time: 45 min

Stems powder of Pongamia pinnata: pH: 3; Equilibration time: 45 min

Ash of stems of Pongamia pinnata : pH:3; Equilibration time: 30 min

SORBENT CONCENTRATION: g/500 ml
SORBENT CONCENTRATION VS 5 REMOVAL OF METHYL ORANGE DYE
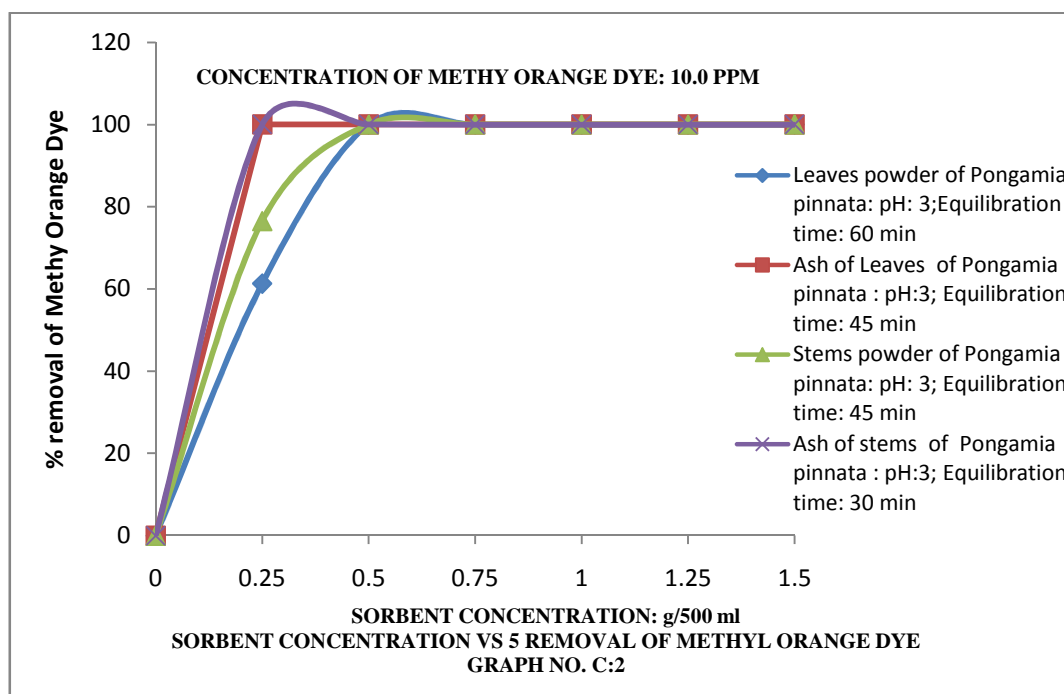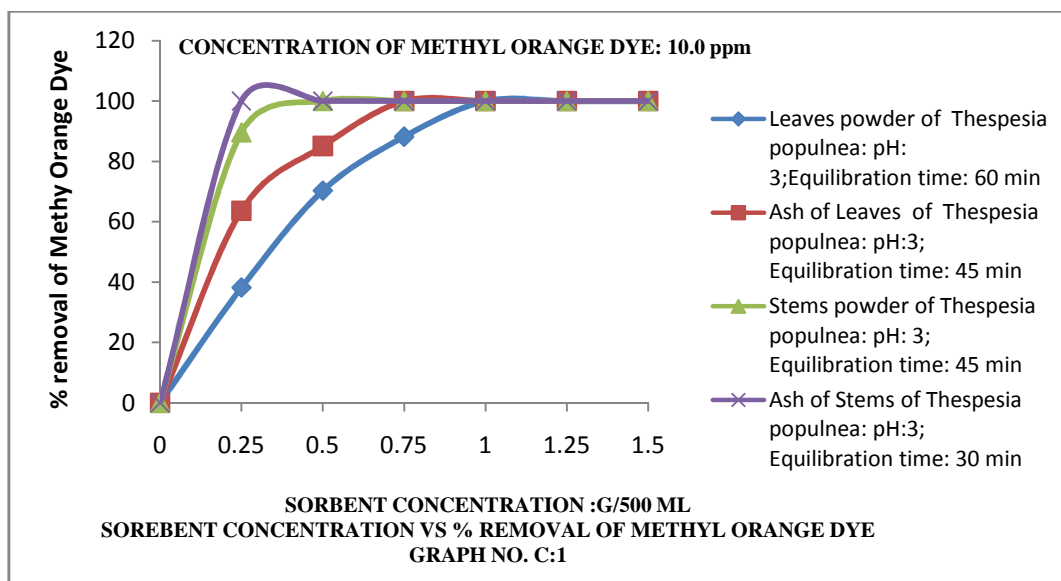GRAPH NO. C:2

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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_4^{2-}	PO_4^{3-}	Cl^-	CO_3^{2-}	NO_3^-	Ca^{2+}	Cu^{2+}	Fe^{2+}	Zn^{2+}	Mg^{2+}
Leaves powder of *Thespesia populnea*	92.0%; pH: 3; 60 minutes; sorbent conc.: 1.0 g/500 ml	10.9	8.0	45.6	13.5	42.1	45.6	40.3	48.0	50.0	43.5
Leaves Ash of *Thespesia populnea*	96.7%; pH:3;45 min; Sorbent conc.:0.75g/500 ml	14.5	8.5	53.2	15.4	48.5	53.5	56.7	52.0	52.3	50.0
Stem powders of *Thespesia populnea*	pH:8; 45 minutes; Sorbent conc.:0.5 g/500 ml	12.4	7.5	49.8	18.0	40.5	56.7	49.0	53.0	56.0	49.0
Stems ash of *Thespesia populnea*	98.0%;pH:3, 30 minutes; Sorbent conc.: 0.25 g/500 ml	13.0	10.3	59.9	19.5	46.3	60.0	57.4	54.5	59.0	54.3
Leaves powder of *Pongamia pinnata*	86.2%; pH:3; 60 minutes; Sorbent conc.:0. 5 g/500 ml.	14.8	6.7	50.4	12.0	41.5	43.0	46.7	44.0	51.0	46.0
Leaves Ash of *Pongamia pinnata*	91.0%; pH:3; 45 minutes; 0.25 gm/500 ml	16.3	7.9	60.1	14.9	47.3	49.0	54.3	59.0	56.0	49.0
Stem powders of *Pongamia pinnata*	96.0%; pH:8; 45 minutes; Sorbent Conc.: 0. 5 g/500 ml	18.7	9.3	56.5	14.0	49.0	50.0	51.0	56.0	59.2	56.0
Stem ash of *Pongamia pinnata*	98.0%; pH:3; 30 minutes; Sorbent Conc.: 0. 25 g/500 ml	19.8	10.0	65.2	16.5	51.0	56.7	52.3	60.0	61.0	59.0

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 *Thespesia populnea* :at pH: 3; Equilibration time: 60 minutes; sorbent conc.: 1.0 g/500 ml	40.5	43.0	45.0	42.0	41.0
Leaves ashes *Thespesia populnea*: at pH: 3; Equilibration time: 45 min; Sorbent conc.:0.5g/500 ml	38.0	52.5	49.0	44.0	49.0
Stem powders of *Thespesia populnea* :at pH:3; Equilibration time: 45 minutes; Sorbent concentration: 0.5 g/500 ml	42.5	44.9	39.9	40.0	48.0
Stems ash of *Thespesia populnea* ::at pH:3; Equilibration time:30 minutes; sorbent concentration: 0.25 gm/500 ml	45.0	54.0	46.5	48.9	47.0
Leaves powders of *Pongamia pinnata* : :at pH:3; Equilibration time: 60 minutes; sorbent concentration: 0. 5 g/500 ml	36.0	45.0	44.5	46.0	46.5
Leaves ash of *Pongamia pinnata* :at pH:3; Equilibration time: 45 minutes; sorbent concentration: 0.25 g/500 ml.	41.0	46.0	50.0	51.0	43.0
Stems powder of *Pongamia pinnata* :at pH:3; Equilibration time: 45 minutes; sorbent concentration: 0. 5 g/500 ml.	49.0	44.0	48.0	45.7	42.0
Stems ash of *Pongamia pinnata* :at pH:3; Equilibration time: 30 minutes; sorbent concentration: 0. 25 g/500 ml.	52.5	47.5	53.0	52.3	46.0

DISCUSSION

With the available data, it is not possible to propose sound theoretical grounds for each observation as further probe is needed on the surface morphology. It is beyond the aims of this work. The surface of the sorbents derived from plant materials, has potential –OH or -COOH groups and their dissociation is pH sensitive. At high pH values, the dissociation of –OH or - COOH groups   impart negative charge to the surface and thereby a thrust for cations prevails on the surface. But as the pH decreases, the –OH or -COOH groups dissociation is less favored and are even

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protinated endowing positive charge to the surface which manifests in the thrust for anions at the surface at low pHs. The protination is expected at pH values less than 3.

The acid dissociation constant of Methyl Orange Dye is: pK: 3.7 and the dye will be changing from quononoid form to benenoid form in the pH range 3.1-4.4 yielding anion on dissociation. The anion of the Dye is expected above pH: 3 (pH = pK ± 1) while un-dissociated form will be present at pH values less than nearly 3.0. 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 showed 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 and thereby adsorption is less. If the pH is further decreased below 3, protination of the sorbent surface occur but the *Dye is in un-dissociated form* and furthermore, the van der Waals interactions and Hydrogen bonding formations between surface and Dye that are responsible for adsorption at such conditions, will be made less effective by the aquated Hydronium ions. *The net result is that around pH: 3 only (nearly), the Dye adsorption towards the adsorbents is effective. Above and below this pH value, the affinity of the sorbent towards the Dye decreases.*

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 film on the sites of adsorbent and thus resulting in decrease in capability of the adsorbent.

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 [47-49] 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 caions have been found to less effect the adsorption of the Dye because at pH: 3, the surface of the of sorbent is protinated and the prevailing positive charge on the surface repels the cations.

4: Applications
The procedures developed in this work have been applied for samples collected from the sewages/effluents of 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 40-50% Methyl Orange Dye can be removed from the waste waters.

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CONCLUSION

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1. Bio-adsorbents derived from plant materials of *Thespesia populnea and Pongamia pinnata* have been found to be effective in extracting Methyl Orange Dye *from polluted waters at pH: 3.*
2. Physicochemical parameters such as pH, time of equilibration and sorbent concentration have been optimized for the maximum removal of Methyl Orange Dye.
3. Fivefold excess of di- and trivalent co-anions are found to be more interfering than monovalent anions with the extraction of the Dye. Cations are less interring.
4. The procedures developed are applied for some industrial samples.

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