International Journal of Engineering Science Invention (IJESI)
ISSN (Online): 2319 – 6734, ISSN (Print): 2319 – 6726
www.ijesi.org || PP. 21-35

Using Bio-Adsorbents Elimination Of Methyl Orange Dye From Polluted Waters

Y. Hanumantha Rao[1], K.A.Emmanuel[2]
[1]*Associate professor, Andhra Loyola College (Autonomous), Vijayawada, Krishna Dist, Andhra Pradesh*
[2]*Associate professor, Sir C R Reddy College (Autonomous), Eluru, W.G.Dist, Andhra Pradesh, India*

Abstract: *Bio-adsorbents derived from plant materials of* ***Aeschynomene aspera and Ficus religiosa*** *have been probed for their surface sorption abilities towards Methyl Orange Dye using simulated waters. The physicochemical parameters such as pH, time of equilibration and sorbent concentrations are optimized for the maximum removal of the Methyl Orange Dye. The extraction is found to be pH sensitive and the affinity of the sorbents towards the dye is high when the pH is nearly 3. Ashes of the bio-materials are more effective in the removal of the dye than raw bio-materials. % of extraction is effected in presence fivefold excess of anions: the interference is of the order: trivalent anion>divalent >monovalent. Co-cations have showed less interference. Themethodologies developed are applied to industrial samples.*

Keywords: Methyl Orange Dye, PollutionControl, Bio-sorbents,Aeschynomene aspera, Ficus religiosa,Applications

I. Introduction

Recent past research in developing pollution control methods, indicates that the sorption nature of Biomasses and bio-wastes of flora or fauna origin are being successfully explored either in their native form or chemically modified form in controlling the polluting ions in wastewaters. 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[1-10]. While probing the biomaterials of different plants for their ability to control dye pollution, we noticed affinity of some dyes towards ***Aeschynomene aspera and Ficus religiosa plants. In the present work the sorbents derived from these plants have been probed.***

In the modern world, the synthetic dyes are being used extensively especially in textile and paper industries. In contrast to the natural dyes, the synthetic dyes are non-degradable to micro-organisms and are toxic[11-13]. So the dyes have to be removed from the wastewaters of dye-based industries and any disposal of sewages without prior treatment for the removal of dyescauses environmental threat and concern.Another potential environmentalproblem with the waters contaminated with dyes is that the colorof the watersblocks the Sun radiation to reach to the aquatic and water-based microorganisms and thereby retards the photochemical reactions in them and as a consequence of this, the environmentally sustainable eco-balance in different eco-systems in disturbed[14].

Environmental researchers are working on developing effective methods for the removal of dyes from wastewaters [15-48]. Different methodologies based on Electro-kinetic coagulation, ion-exchange, membrane filtration, electrochemical oxidation and photo-catalytic degradation process have been developed[15-21] but these methods have one or the other disadvantages, especially non-economical when applied to large scales. In this contest, the researchers are probing the bio-sorbents derived from bio-waste materials for their sorption nature towards the dyes [22-48].

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[49, 50]. Mittal et al [49] studied the removal and recovery of Methyl Orange from wastewaters using waste materials. Chen S et al [50] probed the equilibrium and kinetic aspects of Methyl Orange adsorption on activated carbon derived from *Phragmitesaustralis. Ru Jiang [51] studied the removal of Methyl Orange from aqueous solutions by Maghemite/Chitosan Nanocomposite Films. F. Mogaddasi et al [52] 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 present work is a thorough study on the optimization of extraction conditions such as pH, time of equilibration and sorbent concentration, for the removal of Methyl Orange Dye from polluted waters using biomaterials derived from the leaves and stems of Aeschynomene aspera and Ficus religiosa.

II. Materials And Methods

(A) Chemicals And Reagents: All chemicals used were of analytical grade.**10** ppm solution ofMethyl 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.

(B) Adsorbents:In the present investigation the sorbents derived from ***Aeschynomene aspera and Ficus religiosa have been probed for their sorption nature towards the Methyl Orange Dye.***

A: Aeschynomene aspera B: Ficus religiosa

Fig No. 1: Plants showing affinity towards Brilliant Green Dye

Aeschynomeneaspera is a species of flowering plant in the family of Fabaceae[53]. It is also known by the names ***Sola***, ***Sola Pith Plant***, ***Pith Plant***, ***Laugauni*** *or* ***Netti (Tamil).*** **Pith** of low density from this plant is used to make hats known as pith helmets.

Ficus religiosa is a large dry season-deciduous tree grows up to 30 meters with a large trunk diameter and it has cordate shaped leaves with a distinctive extended tip and it grows well in India. It belongs to Moraceae family. It has many recognized medicinal properties.It is used in various traditional medicines in curing asthma, diabetes, diarrhea, epilepsy, gastric problems, and inflammatory disorders. It has religious sanctity and has the status of "Demi-God" in Hindu, Jain and Buddhist religious texts.

The leaves and stems of ***Aeschynomene asperaand Ficus religiosa***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^{O} 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.

(C)Adsorption Experiment:

Batch system of extraction procedure was adopted [54-56]. 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 dilHCl or dilNaOH 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 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 Brilliant Green 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 fromsimulated 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 theco-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: 3was 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***Aeschynomene asperaand Ficus religiosa***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.***

III. Results And Discussions

The sorption characteristics of the bio-adsorbentshave been studied with respect to various physicochemical parameters. The results are presented in the Graph No. A: 1-8; B: 1&2; C: 1&2.

The following ***observations are significant*****:**

1. % 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 (vide Graph Nos: A: 1-8). At this steady state, rate of adsorption is equal to the rate of desorption.

   With the plant materials of ***Aeschynomene aspera,****% of extractionof Methyl Orange Dye at pH:3 has been found to be 34.5% at 15min, 45.6% at 30 min , 68.4% at 45 min , 75.5% at 60 min or above****for leaves powders (Graph No. A: 1)****; 51.2 at 15 min, 74.5 at 30 min, 83.5 at 45 min and above* ***for leaves ashes*** *(vide Graph No. A: 2****)****; 43.2% at 15 min, 70.1% at 30 minand 84.5% at 45min and above for stems powder (vide Graph No. A: 3); and 65.0% at 15 min, 86.5% at 30 min and above for the ashes of stems (vide Graph No. A: 4).*

   Similarly with the bio-materials of ***Ficus religiosa****, the % of extraction of the Dye at pH:3 has been found to be 30.4 % at 15min, 42.2 % at 30 min , 53.4% at 45 min , 64.5% at 60 min, 70.5% at 75 min or above* ***for leaves powders(vide Graph No. A: 5)****; 48.9% at 15 min, 56.5 at 30 min, 67.9% at 45 min, 74,5% at 60 minor above (vide Graph No. A: 6****) for leaves ashes****; 59.0% at 15 min, 67.5% at 30 min and 73.0% at 45min and above* ***for stems powder*** *(vide Graph No:7); and 56.0 % at 15 min, 78.5% at 30 min and above* ***for the ashes of stems*** *(vide Graph No.8).*

2. **pH sensitivity**: The % of extraction is found to be pH sensitive. *The % removal of the Methyl Orange Dye is more in the pH range 2 to 3 and above and below this pH range, the % removal has been decreasing (Vide Graph No. B: 1 and 2).*

   As for example, in the case of leaves powder of Aeschynomene aspera, the maximum extractability, has been found to be12.3% at pH: 0 (1.0 N HCl); 20.5% at pH:1;63.4% at pH:2; 75.5% at pH:3; 45.9.% at pH:4; 36.5% at pH:5; 23.4% at pH:6; 20.3% at pH:7 and 19.0% at pH:8 while with the ashes of leaves ofAeschynomene aspera, the maximum % removal of the Dye has been found to be: 17.0% at pH:0 (1.0 N HCl), 40.0% at pH:1; 72.3% at pH:2; 83.5% at pH:3; 52.0% at pH:4; 43.4% at pH:5;32.5% at pH:6; 28.0% at pH:7 and 11.0% at pH:8 (vide Graph No.B:1). With the stems powder of Aeschynomene aspera, the % of extraction has been found to be 13.5, 30.1,72.1,84.5,64.5,40.0,36.1, 23.1 and 12.5 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 10.0, 30.1, 75.5, 86.5, 52.0, 43.5, 28.0,23.0 and 14.5 respectively for the same sequence of pHs (vide Graph No: B:1).*

   Similarly with the plant materials of Ficus religiosa, 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*** *: 13.2%, 30.0%, 61.2%, 70.5%, 42.6%, 30.1%, 21.0%, 10.1% and 5.1% for leaves powder; 14.5%, 34.1%, 65.6%, 74.5%, 51.0%, 34.0%, 18.0%,16.0% and 12.0 for leaves ash; 9.5%, 34.5%, 62.0%, 73.0%, 55.2%, 42.3%, 24.5,15.5%*

and12.5%, for stems powder; 11.0%, 38.0%, 69.0%, 78.5%, 63.0%, 35.0%, 29.0%, 22.1% and 13.2% 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 Aeschynomene aspera 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 Aeschynomene aspera plant, the optimum time is found to be 45 min but 30 min is sufficient with their ashes as sorbents. With Ficus religiosa leaves powder as adsorbent, the optimum agitation time has been found to be 75 min but with their ashes, it has been reduced to 60 min; with stems powder of the same plant , optimum equilibration is found to be 60 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 Aeschynomene ***aspera***,plant, the optimum adsorbentconcentration has been found to be :***0.5 gm/500ml for leaves and 0.25 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 ***Ficus religiosa 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 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 % of extraction without co-ions has been found be ranging from 70.5% to 86.0% with the eight sorbents developed in this work but the extraction has been seriously affectedto 15.0% to 29.0% in presence of fivefold excess of SO_4^{2-}; 11.0 to 22.% with Phosphate; and 21.0 to 29.0% with CO_3^{2-}.; with monovalent co-anions, the % of extraction of the dye, has been found to be reduced to 56.0% to 69.0% for Cl^- and 55.0 to 66.0% for NO_3^-

   The co-cations studied viz., Ca^{2+}, Mg^{2+},Fe^{2+},Zn^{2+} *and* Cu^{2+} *have lessinterfered with the % of extraction of the dye. 70.5 to 86.0% extraction of the dye in the absence of the co-ions, has been reduced to 53.0-67.5% in presence fivefold excess of* Ca^{2+}*; 47.8-56.0% for* Cu^{2+} *; 54.0 -65.0% for* Fe^{2+}*; 54.0-63.0% for* Zn^{2+} *and 57.0-63.0% for* Mg^{2+}.

IV. Discussions:

The available data is in adequate to account each observation as it needs thorough probe of surface chemistry using more sophisticated instruments such as Scanning Electron Microscopy (SEM), FT-IR, HRD, Energy Dispersive Spectroscopy (EDX), X-ray Photo Electron Spectroscopy (XPS) before and after adsorption of the dye in addition to the conventional analytical procedures and it is beyond the scope of this study.

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:

At high pH values: Adsorbent-OH $\rightleftharpoons$ Adsorbent-O^- + H^+

Adsorbent-COOH $\rightleftharpoons$ Adsorbent-COO^- + H^+

At low pH values (<pH: 3): Adsorbent-OH + $H^+ \rightleftharpoons$ Adsorbent-O^+H

H

The acid dissociation constant of Methyl Orange Dye is: pK: 3.7 andthe dye will be changing fromquononoid form to benzenoid form in the pH range 3.1-4.4 yieldinganion on dissociation. 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 for the ion-exchange sites of the sorbents and thereby, adsorption is less. If the pH is further decreased below 3, protinationof 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 vander 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 around pH: 3 only the Dye shows affinity towards the sorbents. Increasing or decreasing of the pH (other than optimum pH: 3) , of the equilibrating solution results in the decrease in sorption .

The rate of adsorption is found to be more initially but decreases with time and reaches study 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, therewill not be active sites on the sobent surface for the adsorption process to take place i.e. a saturation station 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 [57-59] 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. Thetrivalent and bivalent anions having more negative charge than mono-valent anions, inhibit the adsorption of anionic Methyl Orange Dye on to the surface of the sorbents whilecaions 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.

V. Applications

The methodologies developed 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 that50-65% Methyl Orange Dye can be removed from the waste waters.

VI. Conclussions

1. Bio-adsorbents derived from plant materials of ***Aeschynomene aspera andFicus religiosa***have been probed for their sorption abilities towards Methyl Orange Dye from polluted waters.
2. Extraction conditions such as pH, sorbent dosage and time of equilibration have been optimized for the maximum removal of Methyl Orange Dye.
3. % removal of the dye is more when the pH of the extraction system is nearly 3.
4. Ashes have been found to more effective than respective raw bio-materials
5. Fivefold excess of di- and trivalent co-anions are found to be interfering markedly while the monovalent anions to a less extent. Co-cations have showed less interference.
6. The procedures developed are applied for some industrial samples.

VII. Acknowledgement:

The authors thank UGC for financial aid.

References

[1] Hanumantharao Y, Medikondu Kishore and Ravindhranath K. ,Characterization and Defluoridation Studies of Active Carbon Derived from Typha Angustata Plants, *Journal of Analytical Science and Technology (JAST)*, 3(2),167**(2012).**

[2] Krishna Veni V. and Ravindhranath K., Chromium (VI) pollution control in waste waters using new bio-sorbents, *ESAIJ*, 7(2), 67**(2012).**

[3] Krishna VeniV. and Ravindhranath K., Extraction of Chromium (VI) from Waste Waters Using Powders and Their Ashes of Barks of *Ficusbenghalensis, Tamarindusindica*and *Acasianilotica*Indica, *Asian J. Research Chem*. 5(2), 225-233**(2012)**.

[4] DivyaJyothi M.,RohiniKiran K. and Ravindhranath K., New Bio-Sorbents in the Control of Phosphate Pollution in Waste Waters, International Journal of Applied Environmental Sciences, 7 (2), 127**(2012)**

[5] DivyaJyothi M., RohiniKiranK. and Ravindhranath K., Phosphate pollution control in waste waters using new bio-sorbents,*International Journal of Water Resources and Environmental Engineering*, 4(4), 73**(2012).**

[6] DivyaJyothi M., RohiniKiranK. and Ravindhranath K., Barks or stems and their ashes of some herbal plants as sorbents in removing phosphates from waste waters, *ESAIJ*, 7(2), 47**(2012).**

[7] Suneetha M. and Ravindhranath K., New bio-sorbents in controlling ammonia pollution in wastewaters, Journal of Chemical and Pharmaceutical Research, 4(1)526**(2012).**

[8] Suneetha M. and Ravindhranath K., Removal of Nitrites from Waste Waters Using Ashes of Some Herbal Plants as Bio-Sorbents, *Research Journal of Science and Technology***,** 4(3), 115**(2012).**

[9] Subba Rao G. V.,Durga Rao S.,Srinivasa Rao R., Appaiah M. and Ravindhranath K., Removal of Chromium (VI) from Polluted Waters Using Biosorbents Derived From Some Herbal Plants, *Journal of Indian Water Works Association*- October-December **(2012)**

[10] Anna ArunaKumari and Ravindhranath K. ,Extraction of Aluminum (III) Ions from Polluted Waters Using Bio-Sorbents Derived from *Acacia Melanoxylon and Eichhornia Crassipes* Plants, *Journal of Chemical and Pharmaceutical Research*, 4(5), 2836 **(2012).**

[11] Leechart , P., Nakbanpote, W. and Thiravetyan P., Application of 'waste' wood-shaving bottom ash for adsorption of azo reactive dye, *J. Environ. Manage*., 90, 912 (**2009).**

[12] Bhatnagar, A., and Jain A.K , A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water, *J. Colloid Interface Sci*., 281, 49 (**2005)**.

[13] Chung, K.T. ,Fulk G.E. and Andrews A.W., Mutagenicity testing of some commonly used dyes, *Appl. Environ. Microbiol*., 42, 641 (**1981)**.

[14] Gao Q Zhang, J. , K. Su, Chen R. and Peng J.,Biosorption of Acid Yellow 17 from aqueous solution by non-living aerobic granular sludge, *J. Hazard. Mater*, 174, 215 (**2010)**.

[15] Laszlo,J.A.,"Preparing an ion exchange resin from sugarcane bagasse to remove reactive Dye from wastewater", Text. Chem. Color., 28(5), 13 (**1996).**

[16] Gemea A. H., Mansour I. A., El-Sharkawy R. G. and Zaki A. B., Kinetics and mechanism of the heterogeneous catalyzed oxidative degradation of indigo carmine.*J. Mol.Catal. Chem.*193 (1-2), 109**(2003).**

[17] Grimau V. L. and Gutierrez M. C.,Decolorization of simulated reactive Dyebath effluents by electrochemical oxidation assisted by UV light. *Chemosphere*. 62, 106**(2006).**

[18] Hachem C., Bocquillon F., Zahraa O. and Bouchy M.,Decolorization of textile industry Wastewater by the photocatalytic degradation process.*Dyes Pigm*. 49 117–125(2001).

[19] Cisneros R. L, Espinoza A. G. and Litter M. I.,Photodegradation of an azo Dye of the textile industry, *Chemosphere*. 48393**(2002).**.

[20] Gupta Suhas V K. Application of low-cost adsorbents for Dye removal—a review.*J. Environ. Manage*. 902313**(2009).**

[21] SrivastavaV., Mall I. D.and Mishra I. M., Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash.,*Chem. Eng. J*. 11779**(2006).**

[22] Namasivayam C., Muniasamy N., Gayatri K., Rani M. andRanganathan K., Removal of Dyes from aqueous solution by cellulosic waste orange peel. Bioresour. Technol.57 37**(1996).**

[23] **Namasi**vayam C., Prabha D. and Kumutha M., Removal of direct red and acid brilliantblue by adsorption onto banana pith.*Bioresour. Technol*. 6477**(1998).**

[24] Gupta V. K., Mittal A., Krishnan L. and Gajbe V., Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash. *Sep. Purif. Technol*. 40. 87**(2004).**

[25] Gupta V. K., Mittal A. and Gajbe V., Adsorption and desorption studies of a water soluble Dye Quinoline Yellow using waste materials. *J. Colloid Interface Sci*. ,284, 89**(2005).**

[26] MittalA., Kurup L., and Gupta V. K., Use of waste materials—bottom ash and de-oiled soya, as potential adsorbents for the removal of Amaranth from aqueous solutions. *J. Hazard. Mater*. 117171–178**(2005).**

[27] McKay G, Ramprasad G and Mowli P P. Equilibrium studies for the adsorption of Dye stuffs from aqueous solution by low cost materials.,*Water Air Soil Pollut*. 29, 273–283**(1986).**

[28] Ramkrishna K. R., Viaraghavan T. Dye removal using low cost adsorbents.,*Water Sci. Technol*. 36, 189–196**(1997).**

[29] Bhattacharya K. G. and Sharma A., Adsorption characteristics of the Dye, Brilliant Green on neem leaf powder.**DyesPigm**. 57, 211–222**(2003).**

[30] Bhattacharya K. G. and Sharma A. Kinetics and thermodynamics of methylene blue adsorption on neem (Azadirachtaindica) leaf powder.**DyesPigm**. 65, 51–59**(2005).**

[31] Kargi F. and Ozmıhc S.,Biosorption performance of powdered activated sludge for removal of different Dyestuffs.,*Enzyme Microb. Technol*. 35, 267–271**(2004).**

[32] Dogan M., Alkan M., Turkyilmaz A. and Ozdemir Y., Kinetics and mechanisms of removal of Brilliant Greeby adsorption on perlite.,*J. Hazard. Mater*. 109, 141**(2004).**

[33] Gong R., Ding Y., Li M, Yang C., Liuan H. and Sun Y. Utilization of powdered peanut hull as biosorbent for removal of anionic Dyes from aqueous solution,*Dyes Pigm*. 64, 187**(2005).**

[34] Mahir A., Sermet C., zkan D. O., and Mehmet D., Removal of reactive blue 221 and acid blue 62 anionic Dyes from aqueous solutions by sepiolite., *Dyes Pigm*. 65(3), 251**(2005).**

[35] Armagan B., Turan M. and Celik M. S., Equilibrium studies on the adsorption of reactive azo Dyes into zeolite. *Desalin.*170, 33 **(2004).**

[36] Kannan N. and Sundaram M. M., Kinetics and mechanism of removal of methylene blue by adsorption on various carbons a comparative study. *Dyes Pigm*. 51, 25**(2001).**

[37] Manju G. N., Raji C. and Anirudhan T. S., Evaluation of coconut husk carbon for the removal of arsenic from water. *Water Res*., 323062 (1998).

[38] Hameed A. H. and EI-Khaiary M. I., Kinetic and equilibrium studies of Malachite green adsorption on rice straw-derived char., *J. Hazard. Mater*. 165, 701**(2008).**

[39] Waranusantigul P., Pokethitiyook P., Kruatrachue M. and Upatham E. S.,Kinetics of basic Dye (methylene blue) bio-sorption by giant duckweed (Spirodelapolyrrhiza). *Environ. Pollut*.,125, 385**(2003).**

[40] Otero M., Rozada F., Calvo L. F., Garcia A. I. and Moran A., Kinetic and equilibrium modeling of Brilliant Greeremoval from solution by adsorbent materials produced from sewage sludges.,*Biochem. Eng. J*. 15, 59 **(2003).**

[41] Jadhav D. N. and Vanjara A. K., Removal of phenol from wastewater using sawdust, polymerized sawdust and sawdust carbon. *Indian J. Chem. Technol*. 11, 35**(2004).**

[42] Bansal M., Singh D. and Gargb V. K., A comparative study for the removal of hexavalent chromium from aqueous solution by agriculture wastes' carbons. *J. Hazard. Mater*.171 83**(2009).**

[43] Jain R and Sikarwar S. Photocatalytic and adsorption studies on the removal of Dye congo red from wastewater. *Int. J. Environ. Pollut*. 27, 158**(2006).**

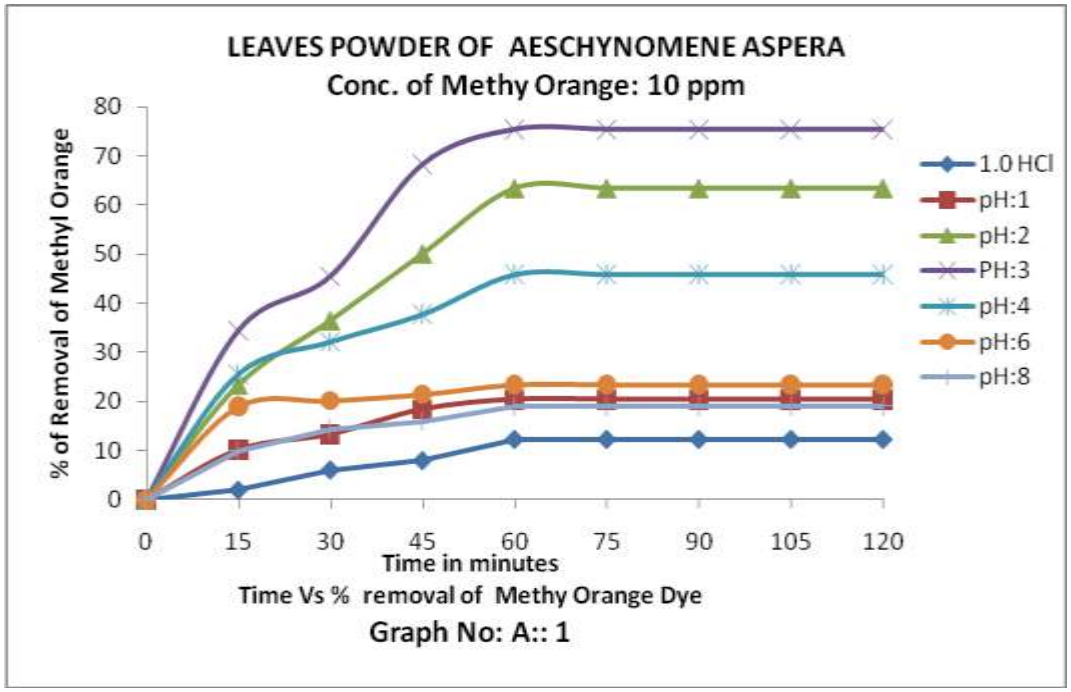
[44] Mall I. D., Upadhyay S. N. and Sharma Y. C. A review on economical treatment of wastewaters, effluents by adsorption,*Int. J. Environ. Stud*. 5177**(1996).**

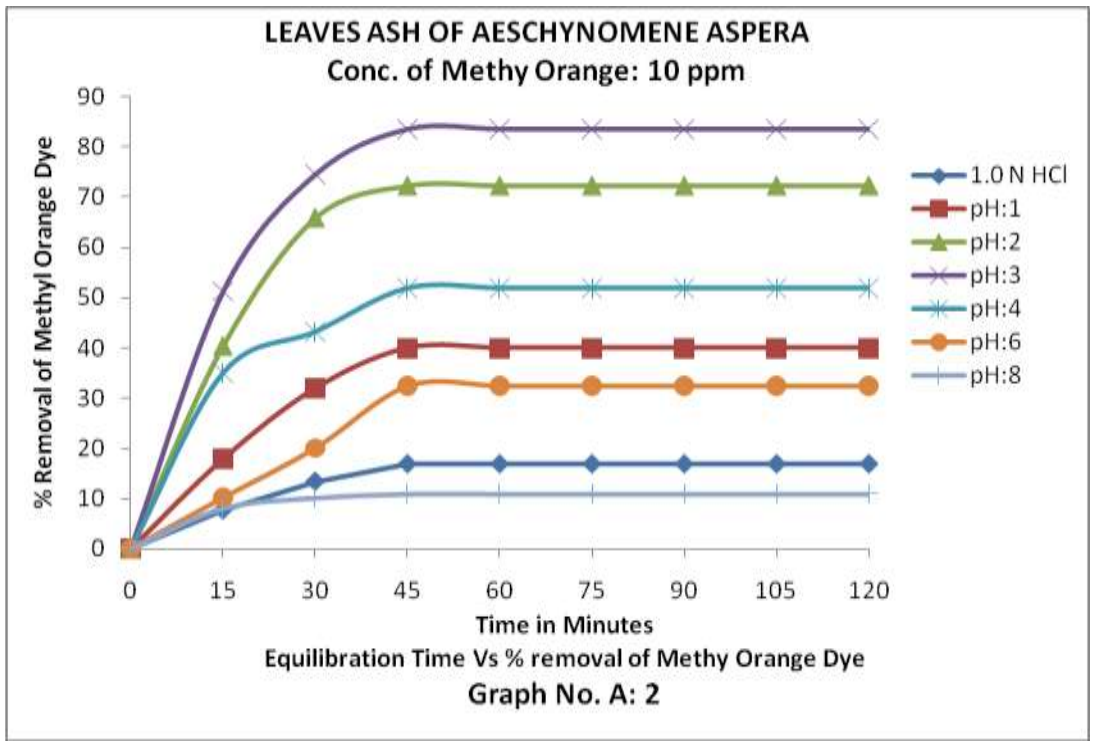
[45] Bailey S. E., Olin T. J., Bricka R. M. and Adrian D. D., A review of potentially low cost sorbents for heavy metals. *Water Res.* 332469**(2009).**

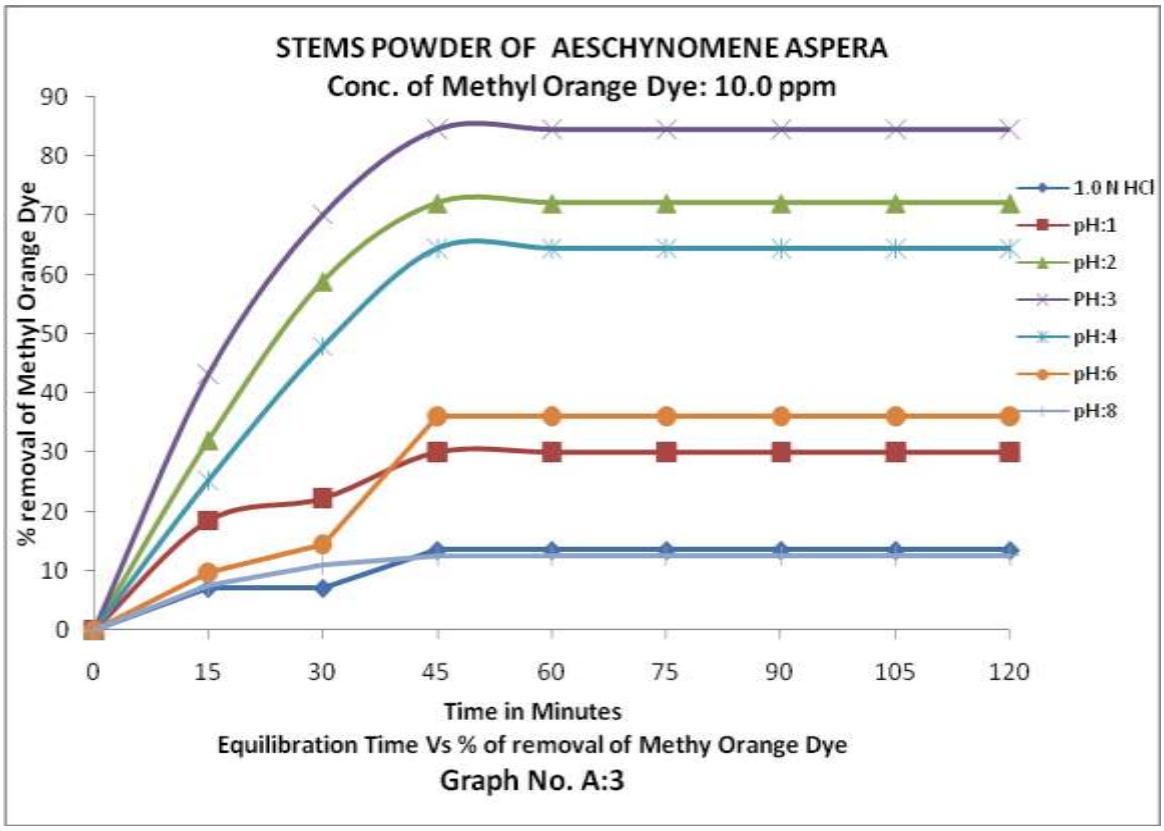
[46] Demirbas A., Agricultural based activated carbons for the removal of Dyes from aqueous solutions: a review. J. Hazard. Mater. 167,1**(2009).**

[47] Garg V. K., Gupta R., Kumar R. and Gupta R.K.. Adsorption of chromium from aqueous solution on treated sawdust. Bioresour. Technol. 92: 79**(2004).**

[48] Shukla A., Zhang Y. H., Dubey P., Margrave J. L. and Shukla S. S., The role of sawdust in the removal of unwanted materials from water. J. Hazard. Mater. 95, 137**(2002).**
[49] Mittal A., Malviya A., Kaur D., Mittal J. and Kurup, L, Studies on the adsorption kinetics and isotherms for the removal and recovery of Methyl Orange from wastewaters using waste materials**,** *J. Hazard Mater* , 148, 229**(2007).**
[50] Chen S., Zhang J., Zhang C., Yue Q., Li Y.and Li E., Equilibrium and kinetic studies of methyl orange and methyl violet ad sorption on activated carbon derived from *Phragmitesaustralis***,** *Desalination*, 252, 149**(2010).**
[51] Ru Jiang, Yong-Qian F, Hua-Yue Zhu, Jun Yao, Ling Xiao, *J Applied Polymer Science*, 125, E540-549**(2012).**
[52] Mogaddasi, MomenHeravi M, Bozorgmehr, R, Ardalan P and Ardalant T, Asian J of Chemistry**,** 22:7, 5093**(2010).**
[53] Friday J. B. and Dana Okano (**April 2006**). *Aeschynomeneaspera (milo)*. The Traditional Tree Initiative. Retrieved 2009-02-20.
[54] Trivedy R. K., Pollution Management in Industries, Environmental Publications, 2nd Ed. Karad, India**(1995**).
[55] Gerard Kiely., Environmental Engineering, McGraw-hall International Editions **(1998).**
[56] Metcalf and Eddy. Wastewater Engineering: Treatment of Reuse. 4th. Ed McGraw Hill Co., New York**, (2003).**
[57] Parks G. A.,*Chem Rev*.**,** 65, 117 (**1965)**.
[58] Parks G.A.,*AdvanChemSer*,No 67,121 (**1967)**.
[59] Ravindhranath K. and Janardhan P.B., *Proc. Indian Natn. Sci. Acad*. 53A, 650 (**1987).**

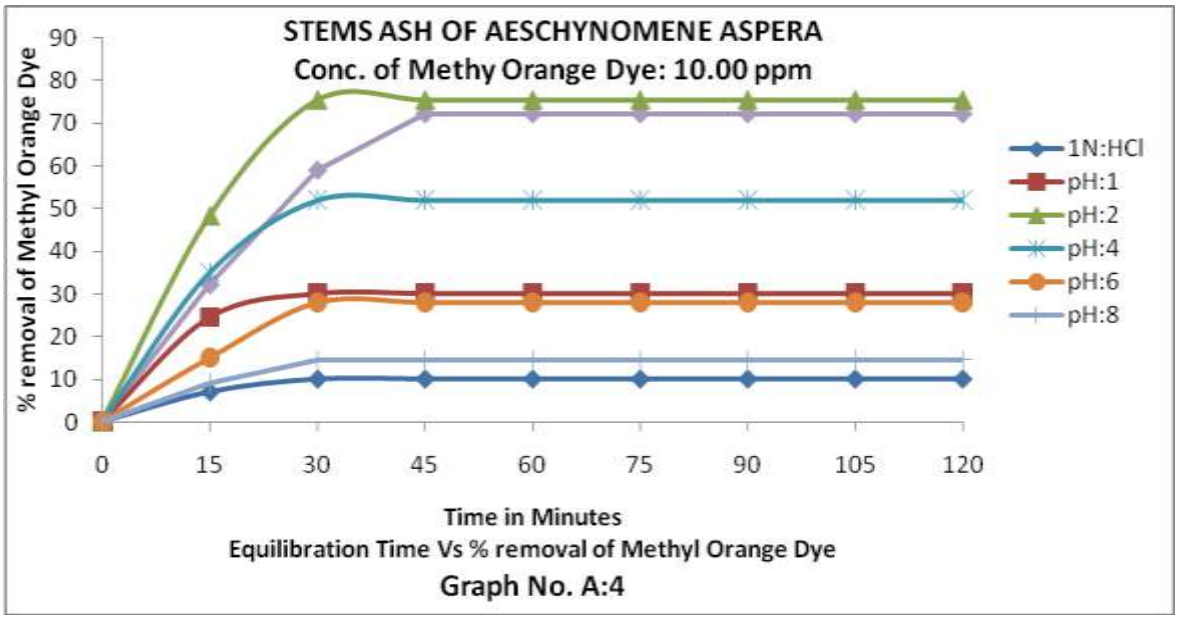

LEAVES POWDER OF AESCHYNOMENE ASPERA
Conc. of Methy Orange: 10 ppm
% of Removal of Methyl Orange
80
70
60
50
40
30
20
10
0
0
15
30
45
60
75
90
105
120
Time in minutes
1.0 HCl
pH:1
pH:2
PH:3
pH:4
pH:6
pH:8
Time Vs % removal of Methy Orange Dye
Graph No: A:: 1


LEAVES ASH OF AESCHYNOMENE ASPERA
Conc. of Methy Orange: 10 ppm
% Removal of Methyl Orange Dye
90
80
70
60
50
40
30
20
10
0
0
15
30
45
60
75
90
105
120
Time in Minutes
1.0 N HCl
pH:1
pH:2
pH:3
pH:4
pH:6
pH:8
Equilibration Time Vs % removal of Methy Orange Dye
Graph No. A: 2



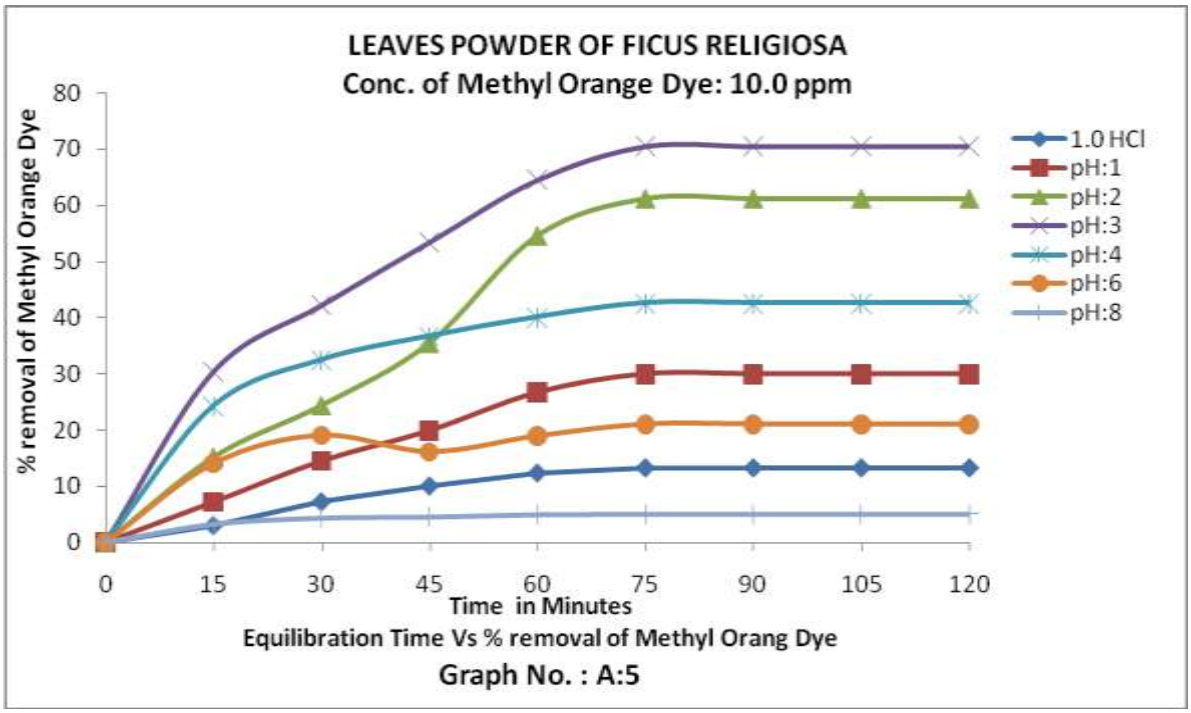
Equilibration Time Vs % of removal of Methy Orange Dye

Graph No. A:3



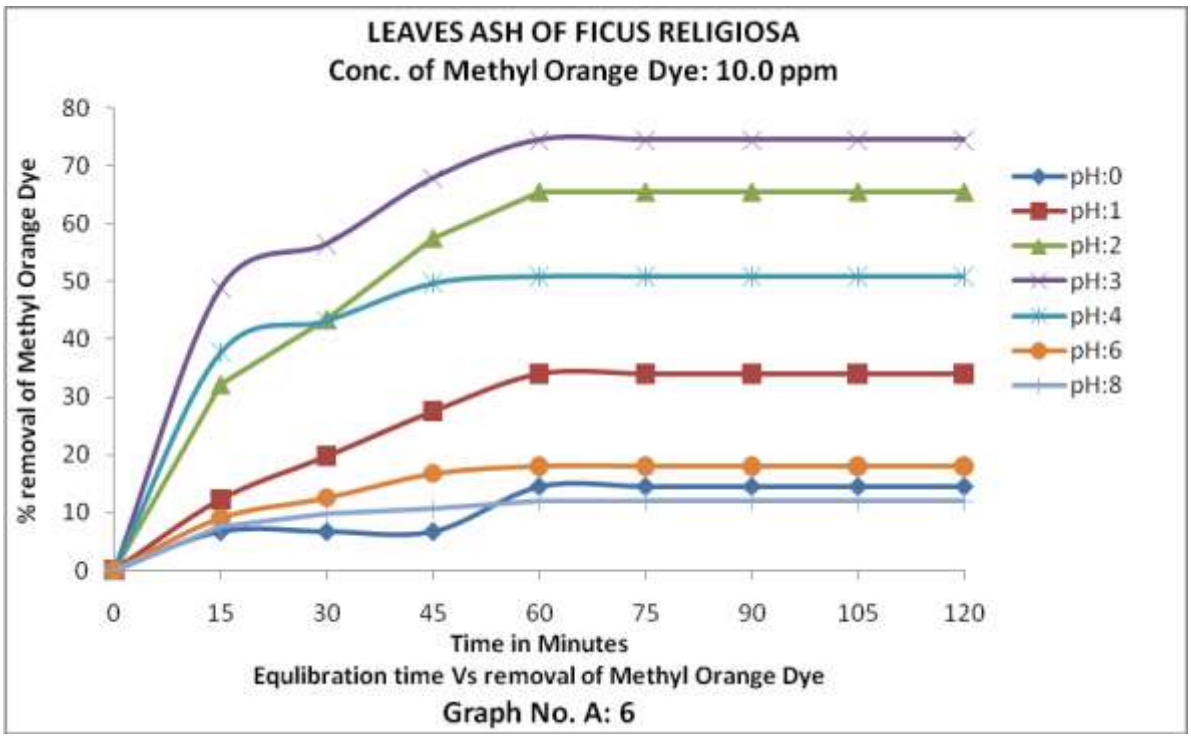
Equilibration Time Vs % removal of Methyl Orange Dye

Graph No. A:4



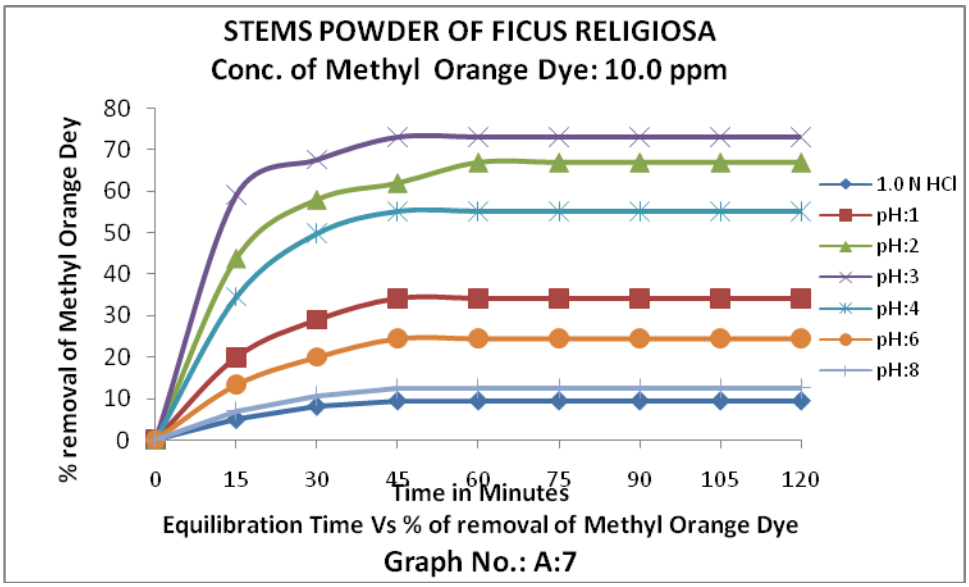
Equilibration Time Vs % removal of Methyl Orang Dye

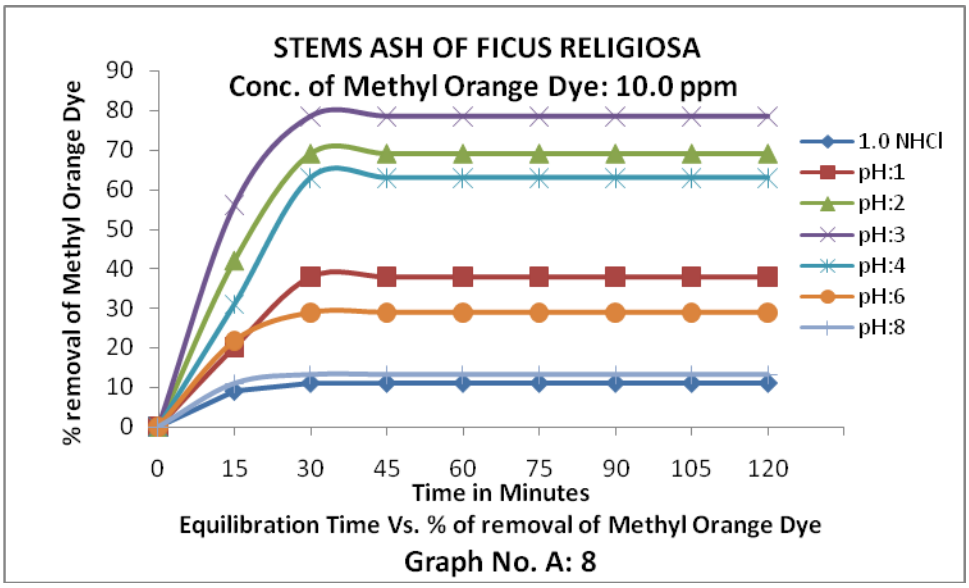
Graph No. : A:5

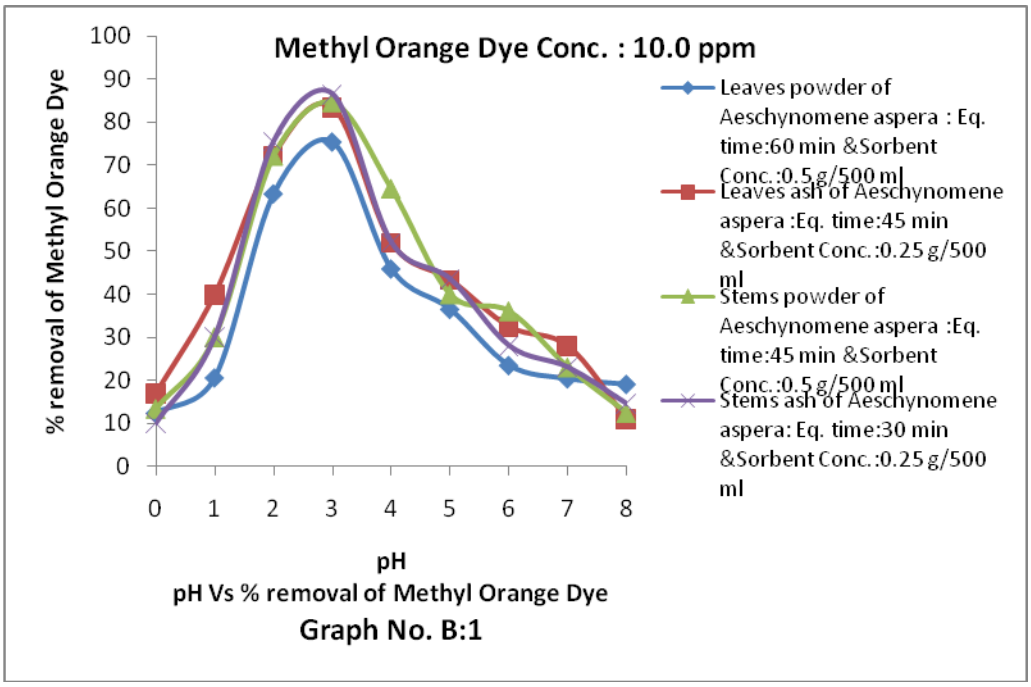


Equlibration time Vs removal of Methyl Orange Dye

Graph No. A: 6

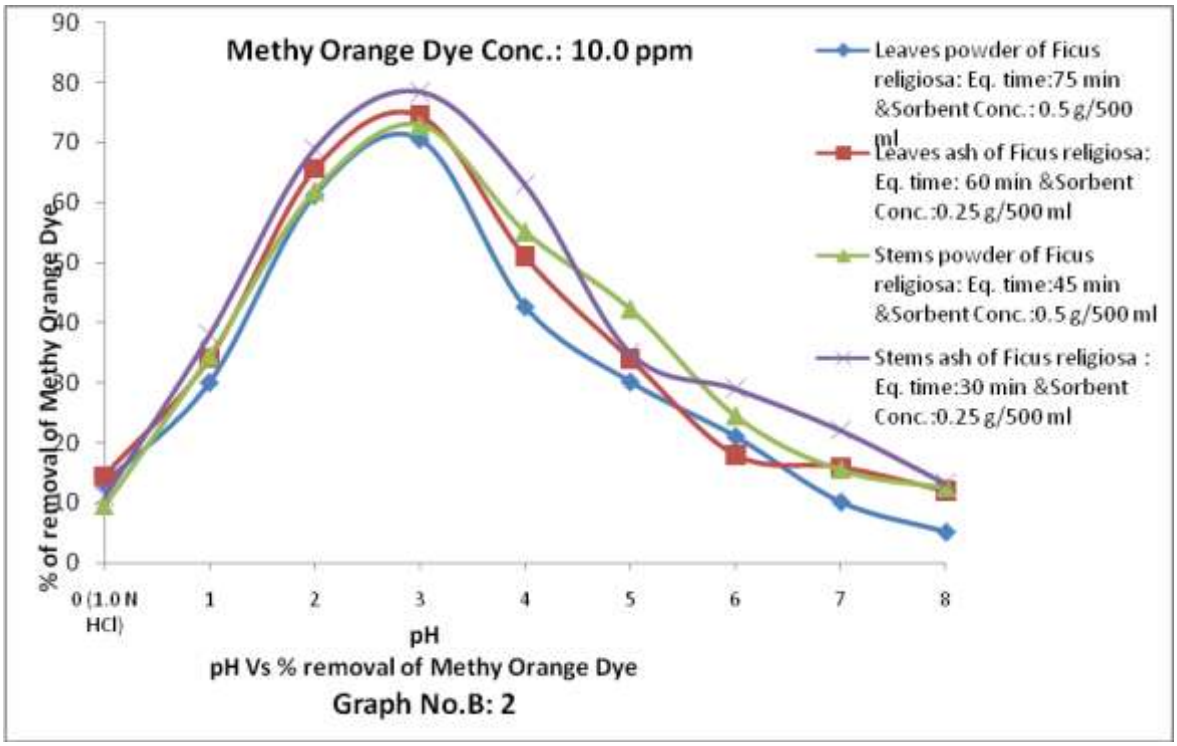

STEMS POWDER OF FICUS RELIGIOSA
Conc. of Methyl Orange Dye: 10.0 ppm
% removal of Methyl Orange Dey
80
70
60
50
40
30
20
10
0
0
15
30
45
60
75
90
105
120
Time in Minutes
1.0 N HCl
pH:1
pH:2
pH:3
pH:4
pH:6
pH:8
Equilibration Time Vs % of removal of Methyl Orange Dye
Graph No.: A:7


STEMS ASH OF FICUS RELIGIOSA
Conc. of Methyl Orange Dye: 10.0 ppm
% removal of Methyl Orange Dye
90
80
70
60
50
40
30
20
10
0
0
15
30
45
60
75
90
105
120
Time in Minutes
1.0 NHCl
pH:1
pH:2
pH:3
pH:4
pH:6
pH:8
Equilibration Time Vs. % of removal of Methyl Orange Dye
Graph No. A: 8



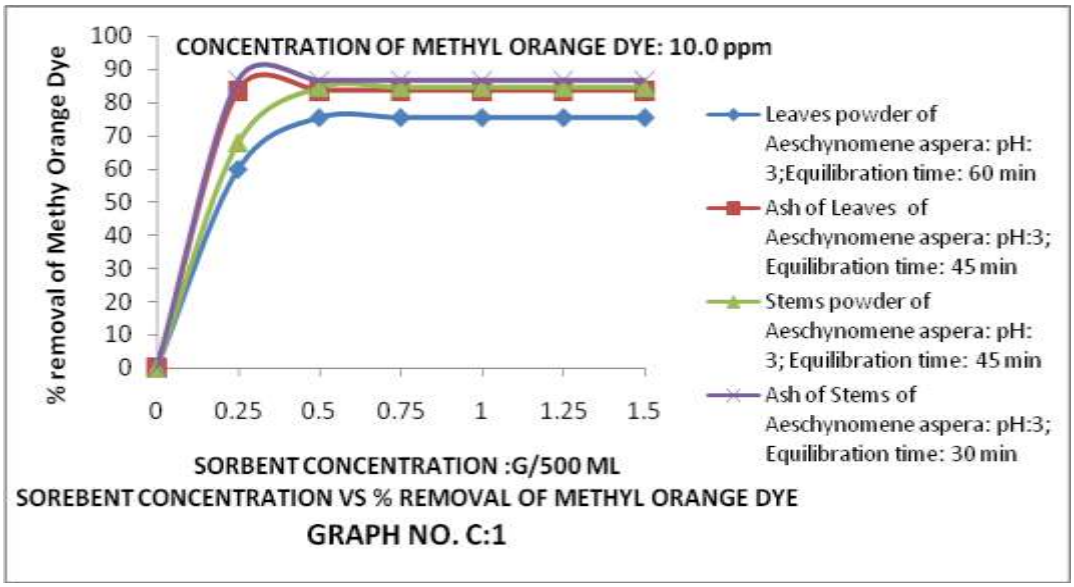
pH Vs % removal of Methyl Orange Dye

Graph No. B:1



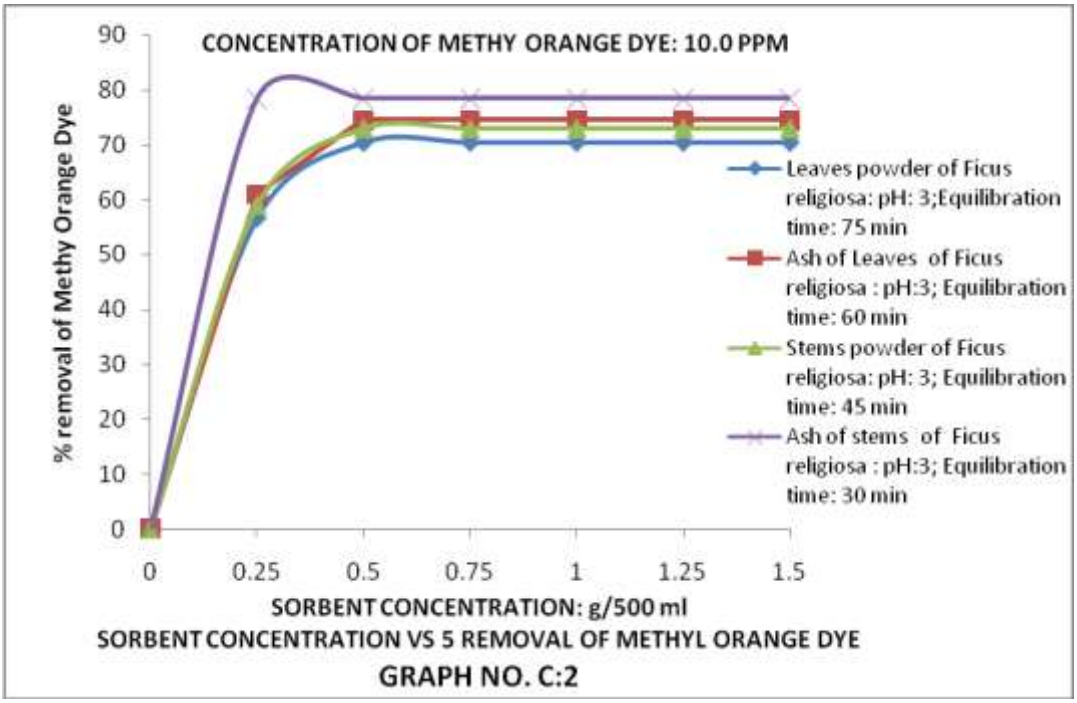
pH Vs % removal of Methy Orange Dye

Graph No.B: 2



SOREBENT CONCENTRATION VS % REMOVAL OF METHYL ORANGE DYE

GRAPH NO. C:1



SORBENT CONCENTRATION VS 5 REMOVAL OF METHYL ORANGE DYE

GRAPH NO. C:2

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 ***Aeschynomeneaspera***	75.5%; pH: 3; 60 mins; sorbent conc.: 0.5 g/500 ml	20.0	11.0	56.0	23.5	62.1	65.0	50.0	58.0	60.0	63.0
Leaves Ash of ***Aeschynomene aspera***	83.5%; pH:3;45 mins; Sorbent Conc.:0.25g/500 ml	24.5	13.5	59.0	25.0	60.0	67.5	52.0	54.0	62.0	60.0
Stem powders of ***Aeschynomene aspera***	84.5%; pH:8; 45 minutes; Sorbent conc.:0.5 g/500 ml	25.0	15.8	64.5	28.0	59.5	62.7	56.0	60.0	59.0	57.0
Stems ash of ***Aeschynomene aspera***	86.5%;pH:3, 30 minutes; Sorbent conc.: 0.25 g/500 ml	22.0	22.0	69.0	29.0	66.0	64.5	54.0	62.0	57.0	59.0
Leaves powder of ***Ficus religiosa***	70.5%; pH:3; 75minutes;Sorbent conc.:0.5 g/500 ml.	18.9	16.7	60.0	22.0	61.5	53.0	53.0	59.5	56.0	61.0
Leaves Ash of ***Ficus religiosa***	74.5%; pH:3; 60 minutes; 0.25 gm/500 ml	29.0	18.9	62.0	24.0	57.3	59.0	49.0	63.5	55.0	58.0
Stem powders of ***Ficus religiosa***	73.0%; pH:8; 45 minutes; Sorbent Conc.: 0. 5 g/500 ml	15.0	19.3	58.0	21.0	59.0	60.0	47.8	64.0	54.0	55.0
Stem ash of ***Ficus religiosa***	78.5%; pH:3; 30 minutes; Sorbent Conc.: 0. 25 g/500 ml	23.0	18.0	65.0	26.0	55.0	58.0	55.0	65.0	63.0	63.0

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 ***Aeschynomeneaspera*** :at pH: 3; Equilibration time: 60 minutes; sorbent conc.: 0.5 g/500 ml	55.5	53.0	65.0	52.0	51.0
Leaves ashes ***Aeschynomeneaspera*** ; at pH: 3; Equilibration time: 45 min; Sorbent conc.:0.25g/500 ml	58.0	58.5	59.0	54.0	59.0
Stem powders of ***Aeschynomeneaspera :***at pH:3; Equilibration time: 45 minutes; Sorbent concentration: 0.5 g/500 ml	52.0	60.0	61.0	60.0	50.0
Stems ash of ***Aeschynomeneaspera :***at pH:3; Equilibration time:30 minutes; sorbent concentration: 0.25 gm/500 ml	60.0	58.0	59.0	63.5	57.0
Leaves powders of ***Ficusreligiosa:*** :at pH:3; Equilibration time: 75 minutes; sorbent concentration: 0. 5 g/500 ml	53.0	55.0	58.5	61.0	51.5
Leaves ash of ***Ficusreligiosa*** :at pH:3; Equilibration time: 6 minutes; sorbent concentration: 0.25 g/500 ml.	51.0	56.0	57.0	63.0	57.0
Stems powder of ***Ficusreligiosa:***at pH:3; Equilibration time: 45 minutes; sorbent concentration: 0. 5 g/500 ml.	56.0	54.0	58.0	65.0	55.0
Stems ash of ***Ficusreligiosa***:at pH:3; Equilibration time: 30 minutes; sorbent concentration: 0. 25 g/500 ml.	62.0	57.5	60.0	55.0	60.5