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Leaves and Barks of Some Plants as Bio-Adsorbents in the Control of Methylene Blue Dye from Waste Waters

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Abstract : Leaves and stems/barks of Phyllanthus Neruri, Moringa Tinctoria, Tridox Procumbens and Ficus religiosa plants have been probed for their sorption abilities towards Methylene Blue using simulated polluted waters. At high pH values, these sorbents are found to be effective. The physicochemical parameters such as pH, time of equilibration and sorbent concentrations are optimized for the maximum removal of Methylene Blue. Methodologies have been developed for the extraction of good quantities of Methylene Blue. More than 90% removal of Methylene Blue has been found to be possible with simulated waters at optimum conditions of extractions. Fivefold excess of anions have not interfered. Cations like Ca^{2+}, Cu^{2+}, and Mg^{2+} have interfered to some extent while Cations like Fe^{2+} and $Zn^{2+}$are synergistically maintained the complete extraction of the dye. The procedures developed are successfully applied to the industrial effluents.

Key Words: Methylene Blue; pollution control; bio-adsorbents; applications.

1: Introduction

In the recent past, much research interest is being devoted to evoke sorption potentialities of the waste materials of flora and fauna origin either in their native state or chemically modified form in controlling the hazardous polluting ions in waste waters. 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.

Dyes are being extensively used in industries based on textile, paper, plastic and cosmetics. The effluents from these industries possess considerable amounts of dyes [1]. The dumping of industrial wastes without the complete removal of the dyes form the effluents, is leading to the contamination of nearby water bodies with dyes [2-4]. Most of the synthetic dyes are recalcitrant and are resistant to bio-degradation [5] and are accumulated in the water bodies causing potential threat to aquatic life due to the toxic nature of them or their oxidation products [4]. Further, the color in waters beside being aesthetically unpleasant, will not allow the radiation to reach the bio-materials and thereby, some of the photo-induced reactions, which are essential for sustaining life, are slowed down or even averted. Thus the presence of dyes even in traces is causing concern due to toxicological and environmental reasons [2, 3].

Methylene Blue is an important dye and finds applications in coloring of paper, cottons, and wools and in preparing hair colorants and it is hazardous to human beings causing the rise in heartbeat, vomiting, shock, cyanosis, jaundice, quadriplegia, tissue necrosis and even cancer [4, 5].

The conventional wastewater treatment such as aerobic biodegradation has low removal efficiency for these dyes. Methods based on ***Physical and Chemical process*** such as chemical oxidation, coagulation, or filtration and membrane separation ***are costly*** [6, 7]. The ***adsorption processes*** using active carbons are proving to be ***effective*** in the removal of dyes from waste waters but they are ***expensive*** [8-11].

The use of the bio-waste materials for the removal of synthetic dyes from waste waters is less trodden [12-24]. There are some attempts to remove Methylene Blue from waste water using activated and non-activated bentonites [7], sand [13], bamboo-based activated carbon [21], gypsum [22], treated olive pomace and charcoal [23], water hyacinth [24]. These methods suffer from one or the other disadvantage and universally acceptable eco-friendly procedures are still evading the researchers.

We made some progress in this aspect in developing successful procedures for the removal of some potential polluting ions and they have been reported to the Literature [25-31].

In the present work, the sorption characteristics of powders of leaves, stems or barks of different plants have been probed for their adsorption abilities towards Methylene Blue ions from polluted waters by optimizing the various physicochemical parameters such as pH, time of equilibration, sorbent concentration and presence of some common interfering ions using simulated waters. Thus developed methodologies are endeavored to apply to the actual industrial wastes.

2: Materials and Methods

A: Chemicals : All chemicals used were of analytical grade.

Stock solution of Methylene Blue**:** 50 ppm of Methylene blue solution was prepared by dissolving a requisite amount of A.R. grade Methylene Blue dye in double distilled water. It was suitably diluted as per the need.

B: Adsorbents: *Sorbents pertaining* to ***Phyllanthus Neruri, Tridox Procumbens, Moringa Tinctoria and Ficus religiosa*** have been found to have affinity towards Methylene Blue.

Phyllanthus Niruri ***Tridax procumbens*** ***Morinda tinctoria*** ***Ficus religiosa***

Fig. 1: Plants showing affinity towards Methylene Blue Dye

Phyllanthus Niruri is an herbal plant belonging to ***Phyllanthaceae*** family and is found in Central and Southern India. It has many therapeutic values in curing jaundice, diabetes, dyspepsia, ulcers, sores, swellings, ophthalmia and chronic dysentery. ***Tridax procumbens*** is a species of flowering plant in the daisy family and is best known as a widespread weed and pest plant. It grows worldwide in tropical, subtropical and mild temperate regions. It possesses medicinal uses especially for diabetic treatment [32]. ***Morinda tinctoria***, commonly known as ***Aal or Indian Mulberry*** is a species of flowering plant and belongs to ***Rubiaceae family*** and is native to South Asia. It is an evergreen shrub growing to 5-10 m tall. The plant is extensively cultivated in India and its leaves and roots are used in traditional system of medicine, as astringent, deobstrent, emmengogue and to relieve pain in the gout. [33] It is reported to have anticonvulsant activity [34]. ***Ficus religiosa***, or **Bo-Tree** is large dry season-deciduous or semi-evergreen tree grow up to 30 meters. It is a species of banyan fig native to South Asia and belongs to the Moraceae family and is considered as sacred by Hindus and Buddhists.

Sorbent Preparation: The leaves or barks or stems of the plants were cut freshly, washed with tap water, then with distilled water and then sun dried. The dried materials were powdered to a fine mesh of size: <75 microns and activated at 105^o C in an oven and then employed in this study.

C: Adsorption Experiment:

Batch system of extraction procedure was adopted [35-37]. Carefully weighted quantities of adsorbents were taken into previously washed one lit/500 ml stopper bottles containing 500ml/250ml of Methylene Blue 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, filtered and was analyzed for Methylene Blue spectrophotometrically. The dye has λmax at 661 nm and obeys Beers-Lambert's law at low concentrations. The O.D. measurements were made at the said λmax using UV-Visible Spectrophotometer (Systronics make) [12]. The obtained O.D value for the un-known solution was referred to standard graph (drawn between O.D and Concentration) prepared with known amounts of Methylene Blue by adopting method of Least Squares to find concentration of Methylene Blue in unknown solutions.

The sorption characteristics of the said adsorbents were studied with respect to the time of equilibration, pH and sorbent dosage. At a fixed sorbent concentration, the % removal of Methylene Blue from sample waters was studied with respect to time of equilibration at various pH values. The results obtained were presented in the Graph Nos. A: 1-6. To fix the minimum dosage needed for the maximum removal of the Methylene Blue ions 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. B: 1 and 2.

D: Effect of other Ions (Interfering Ions):

The interfering ions chosen for study were the common ions present in natural waters viz. Sulphate, Fluoride, Chloride, Nitrate, Phosphate, Carbonate, Calcium (II), Magnesium (II), Copper(II), Zinc(II) and Nickel (II). The synthetic mixtures of Methylene Blue and of the foreign ions were so made that the concentration of the foreign ion was maintained at fivefold excess than the dye concentrations as cited in the Table: 1. 500 ml 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 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 Methylene Blue concentration. % of extraction was calculated from the data obtained. ***The results were presented in the Table: 1.***

E: Applications of the Developed Bio-Sorbents:

The new methodologies developed in this work were applied for the removal of the dye from real sewage/effluent samples collected from some dyeing industries at Hyderabad and Mangalore. For this purpose, samples were collected from the effluents of industries and the samples were analyzed for actual amounts of Methylene blue and then the samples were fed with known amounts of Methylene blue.

Then these samples were ***subjected to the extraction for the dye using the bio-sorbents developed in this work at optimum conditions of extraction. The results obtained were presented in the Table 2.***

Table No. :1: Effect of interfering Ions on the Extractability of Methylene Blue with different Bio-sorbents

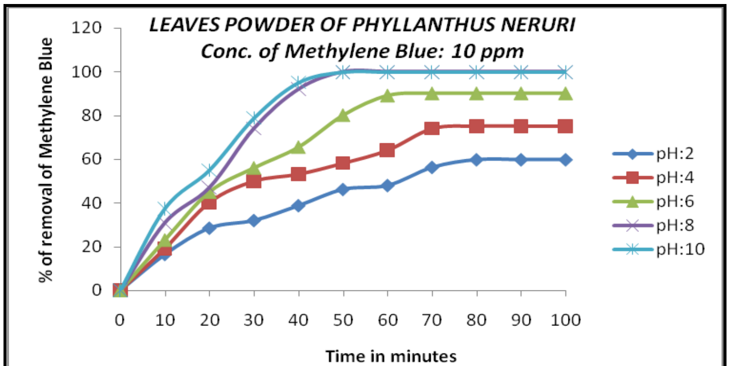
S.No	Adsorbent and its concentration	Maximum Extractability at optimum conditions	*Extractability of Methylene Blue in presence of fivefold excess of (50 ppm) interfering ions at optimum conditions: Conc of Methylene Blue: 10 ppm*									
			SO_4^{2-}	PO_4^{3-}	Cl^-	CO_3^{2-}	F^-	Ca^{2+}	Cu^{2+}	Fe^{2+}	Zn^{2+}	Mg^{2+}
1	Leaves powder of ***Phyllanthus Neruri***	100.0%; pH: 8;50 min.; sorbent conc.: 1.0 g/l	98.5%	98.1%	100.0%	100. 0%	98.5%	90.2%	93.5%	100.0%	100.0%	92.2%
2	Stems powder of ***Phyllanthus Neruri***	100.0%; pH:8; 40 min.; sorbent conc.:1.0 g/lit	99.0%	98.0%	99.5%	100. 0%	99.5%	91.2%	90.0%	100.0%	100.0%	93.5%
3	Leaves powders of ***Moringa Tinctoria***	100.0%; pH:8; 60 min.; Sorbent conc.:1.5 g/lit	98.7%	99.0%	100.0%	100. 0%	90.0%	92.02%	91.6%	100.0%	100.0%	94.6%
4	Stems powder of ***Moringa Tinctoria***	100.0%;pH:8, 40 min.; Sorbent conc.: 1.0 g/l	100.0%	98.0%	100.0%	100. 0%	97.9%	89.0%	92.5%	100.0%	98.5%	93.5%
5	Leaves powder of ***Tridox Procumbens***	100.0%; pH:8; 50 min.; Sorbent conc.:1.0 g/lit.	97.0%	98.5%	96.5%	97.0%	96.5%	88.0%	88.3%	100.0%	99.0%	89.0%
6	Stems powder of ***Tridox Procumbens***	100.0%; pH:8; 30 min; Sorbent Conc.: 0.75 g/l	97.9%	98.5%	100.0%	100. 0%	97.0%	87.9%	92.5%	100.0%	99.5%	92.5%
7	Leaves powders of ***Ficus religiosa***	100.0%; pH:8; 50 min.; Sorbent Conc.: 1.5 g/l	97.0%	97.5%	100.0%	100. 0%	96.5%	90.5%	93.8%	100.0%	99.2%	92.8%
8	Stems powder of ***Ficus religiosa***	100.0%; pH:8; 30 min.; Sorbent Conc.: 1.0 g/l	93.7%	95.5%	96.0%	96.9%	95.5%	92.0%	94.0%	100.0%	98.8%	93.5%

Table No.2: % of Extractability of Methylene Blue from different Industrial Effluents with Bio-Sorbents developed in this work

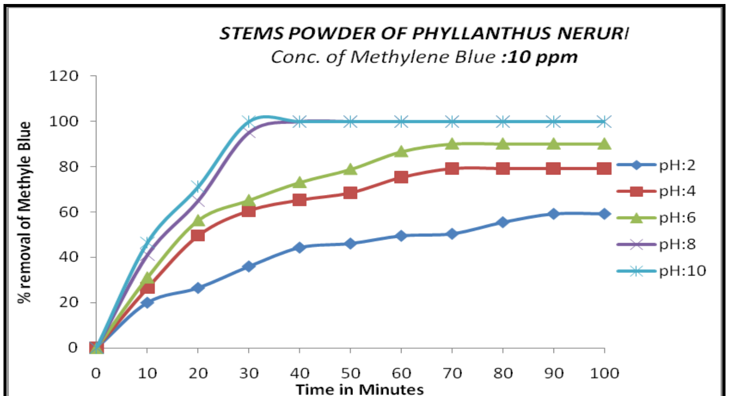
Bio-Sorbent	**% of Extractability of Methylene Blue**				
	Sample 1: Fed with 10.0 ppm of Methlene Blue	**Sample 2 Fed with 15.0 ppm of Methlene Blue**	**Sample 3 Fed with 20.0 ppm of Methlene Blue**	**Sample 4 Fed with 25.0 ppm of Methlene Blue**	**Sample 5 Fed with 30.0 ppm of Methlene Blue**
Leaves powders of ***Phyllanthus Neruri*** :at pH:8; Equilibration time: 50 min. and sorbent concentration: 1.5 g/l	93.5%	94.5%	93.0%	92.5%	95.0%
Stems powder of ***Phyllanthus Neruri*** : at pH:8; Equilibration time: 40 min. and sorbent concentration: 1.0 g/l	94.0%	93.5%	92.5%	90.5%	95.6%
Leaves powders of ***Moringa Tinctoria*** :at pH:8; Equilibration time: 60 min. and sorbent concentration: 1.5 g/l	95.5%	96.5%	93.5%	97.0%	96.0%
Stems powders of ***Moringa Tinctoria*** :at pH:8; Equilibration time: 40 min. and sorbent concentration: 1.0 g/l	97.0%	92.0%	95.7%	94.5%	92.5%
Leaves powders of ***Tridox Procumbens*** :at pH:8; Equilibration time: 50 min. and sorbent concentration: 1.0 g/l	90.5%	89.5%	87.8%	86.9%	92.0%
Stems powder of ***Tridox Procumbens*** : at pH:8; Equilibration time: 30 min.and sorbent concentration: 0.75 g/l	95.0%	93.5%	93.4%	92.3%	91.6%
Leaves powders of ***Ficus religiosa*** :at pH:8; Equilibration time: 50 min. and sorbent concentration: 1.5 gms/l	94.0%	93.0%	92.3%	93.6%	91.9%
Stems powder of ***Ficus religiosa*** :at pH:8; Equilibration time: 30 min. and sorbent concentration: 1.0 g/l	92.9%	93.5%	90.0%	92.3%	97.9%

3: Results and Discussions

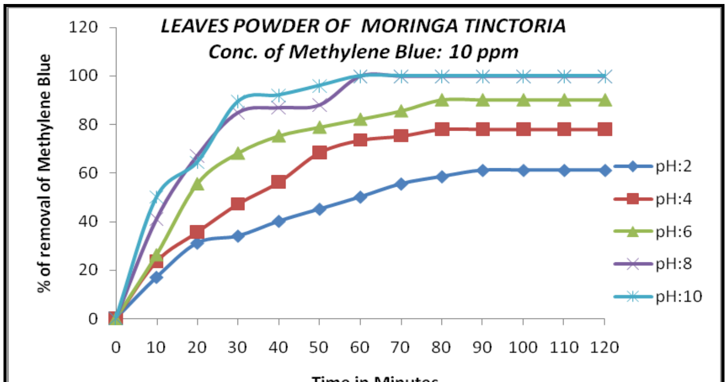
The extractability of Methylene Blue with the sorbents derived from plant materials of ***Phyllanthus Niruri, Tridox Procumbens, Moringa Tinctoria and Ficus religiosa*** *have been studied with* respect to various physicochemical parameters such as *pH, time of equilibration and sorption concentration* and the results obtained are presented in the Graph No. A: 1-8; B: 1 &2 and C:1 & 2. The following observations are significant:



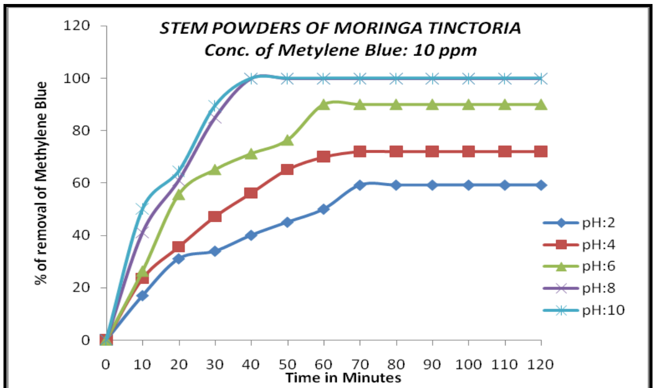
Equilibration Time Vs % of removal of Methylene Blue
Graph No.: A :1



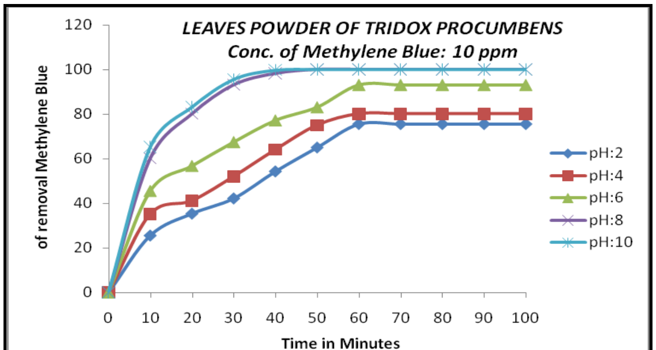
Stems Powder of Phyllanthus Neruri
Graph No.: A:2



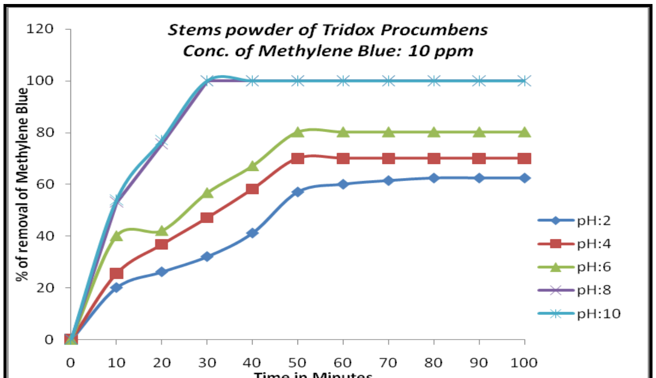
Equilibration Time Vs % of removal of Methylene Blue
Graph No.: A: 3



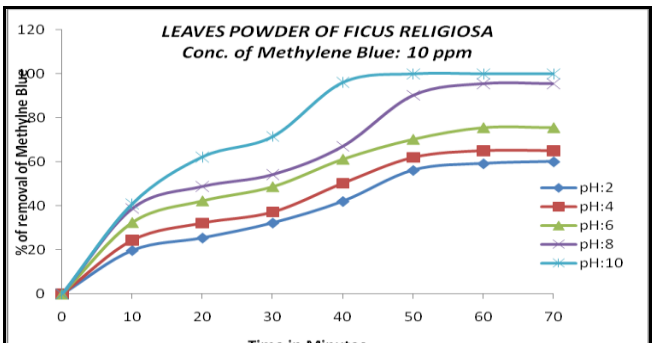
Equilibration Time Vs % of removal of Methylene Blue
Graph No.: 4



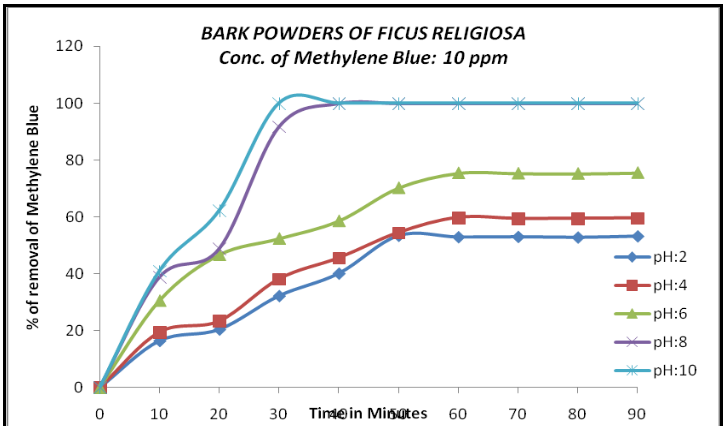
Equilibration Time Vs % of removal of Methylene Blue
Graph No.: A:5



Equilibration Time Vs % of removal of Methylene Blue
Graph No.: A:6

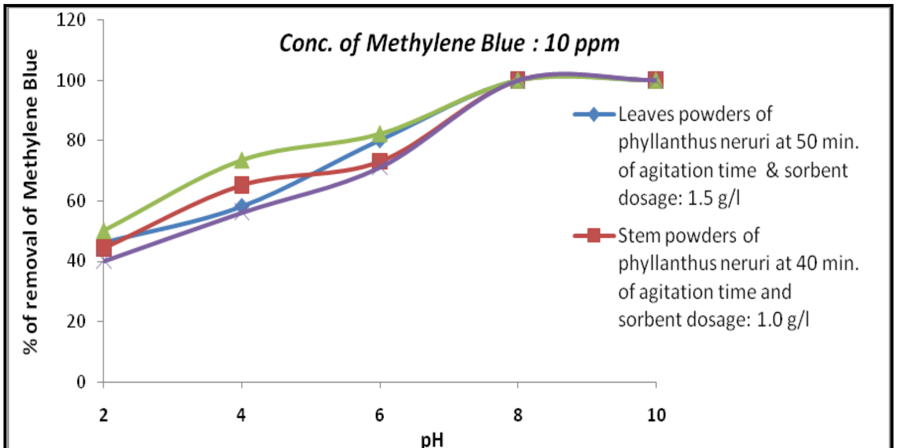


Equilibration Time Vs % of removal of Methylene Blue
Graph No.: 7



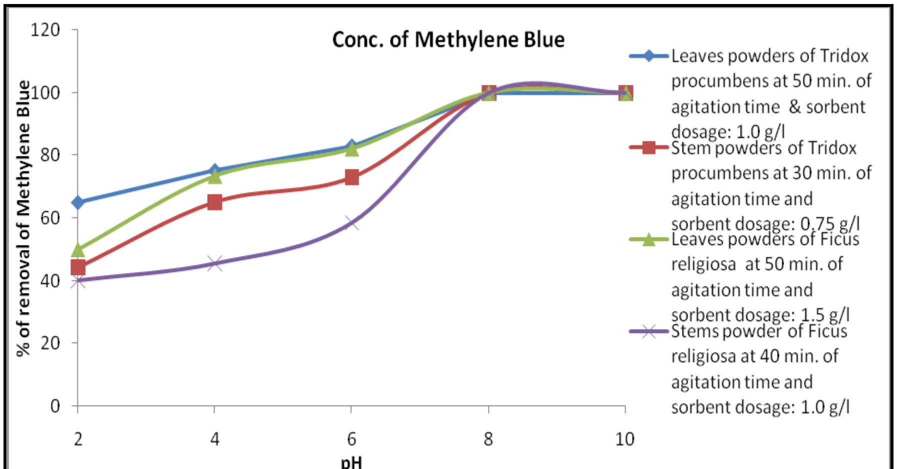
Equlibration Time Vs % of removal o f Methylene Blue

Graph No.: A:8



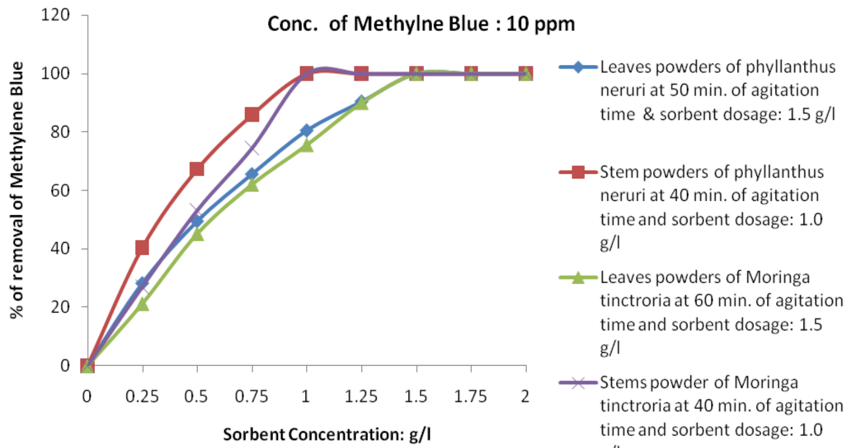
pH Vs % removal of Methylene Blue

Graph No.: B:1

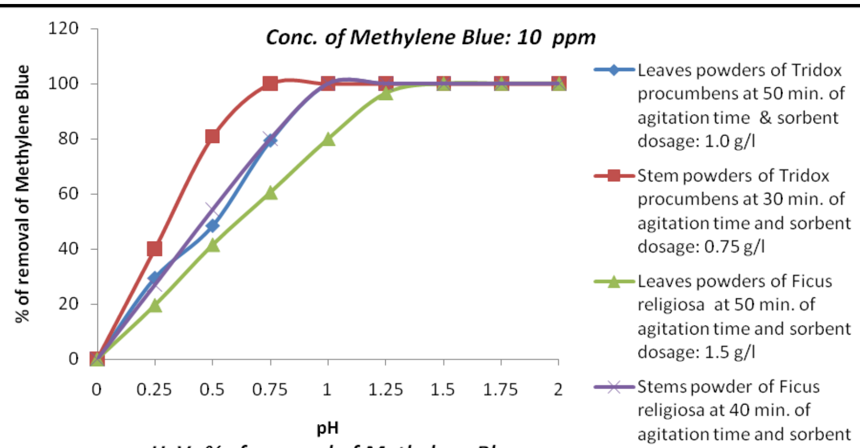


pH Vs % of removal of Methylene Blue

Graph No.: B:2



Sorbent Dosage Vs % of removal of Methylen Blue
Graph No.: C:1



pH Vs % of removal of Methylene Blue
Graph No.: C:2

1. Time of equilibration: Percent of extractability increases with time for a fixed adsorbent at a fixed pH and after certain duration, the extractability remains constant, i.e. an equilibrium state has been reached. In other words, there will not be any further adsorption after certain time of equilibration time (vide Graph Nos. A: 1-8). As for example, in the case of powders of leaves of Phyllanthus Niruri, % of extraction of Methylene Blue has been found to be 31.0% at 10 min, 47.1% at 20 min, 74.2% at 30 min, 92.1% at 40 min and 100% at 50 min or more at pH: 8. The same trend is found in other sorbents.

2. Effect of pH: The removal of Methylene Blue has been found to be increasing with the increase of pH of the agitating solution for a fixed adsorbent at an optimum time of agitation (Vide Graph No. B: 1 and 2 and also Graph Nos. A: 1-8)). For example , the maximum extractability has been found to be 46.2% at pH: 2; 58.2% at pH: 4; 80.2% at pH: 6; 100% at pHs: 8 and 10 after an equilibration period of 50 minutes for the powders of Phyllanthus Niruri leaves as sorbent (vide Graph No. A: 1). With the stems powder Phyllanthus Niruri, the % of extraction has been found to be 44.3% at pH: 2; 65.2% at pH: 4; 73.1% at pH: 6 and 100% at pH: 8 and 10 after an equilibration time of 30 minutes (vide Graph No.A:2). Similarly at pHs 2, 4, 6, 8 and 10, the % of extractions have been found to be respectively 50.1%, 73.5%, 82.2%, 100% and 100% after 60 minutes of agitation time for Leaves powder of Moringa tincroria and 40.1%, 56.2%, 71.2%, 100% and 100% after 40 minutes of agitation time for stem powders of Moringa tincroria (vide Graph No.A:3 and 4).

In the case of leaves powder of Tridox procumbens, the % of extractability of Methylene Blue dye has been found to be 64.9% at pH:2; 75.1% at pH:4; 83.0%at pH:6 and 100% at pH:8 and 10 at 50 minutes of agitation and with 1.0 g/l of sorbent dosage (vide Graph No.:A:5; C:2) while with its stem powders, the % of extraction has been found to be 32.1%, 47.1%, 56.7% and 100% at the respective pHs and with a reduced sorbent concentration of 0.75g/l (vide Graph No.A:6 and C:2).

With leaves powder of Ficus religiosa, % of removal of Methylene Blue dye has been found to be 56.2%, 62.1%, 70.2%, 90.3% and 100.0% at the respective pHs of 2, 4, 6, 8 and 10 with the sorbent dosage of 1.5 g/l while with the bark powders of the same plant, 40.2%, 45.6%, 58.6% and 100% of extractions have been found at the respective pH values and with a sorbent concentration of 1.0 g/l (vide Graph No. A: 7 and 8 and C: 2).

3. Time of equilibration: In most of the bio-sorbents, the equilibration time needed for the maximum extractability of Methylene Blue has been found to be less for leaves powder than with stem/bark powders. As for example, the optimum equilibration time is 50 min for leaves of Phyllanthus neruri while it is 40 minutes for their stems powder; 60 minutes for leaves powder and 40 minutes for stems powder in the case of Moringa tinctroria; and 50 minutes for leaves powder and 30 minutes only for stem powders in the case of Tridox procumbens. Leaves powder of Ficus religiosa extracts maximum dye at 50 minutes of agitation time while the bark powders of the same plant needs only 30 minutes of agitation at the optimum conditions of extraction (Graph No.A:1-8).

4. Sorbent Concentration: The optimum sorbent concentration required for the maximum extractability of the Methylene Blue is found to be less for stem/bark powers than leave powders. The optimum

5. concentration has been found to be: 1.5 g/l for leaves powder and 1.0 g/l for stem powders in case of Phyllansthus neruri plant; 1.5 g/l for leaves powder and reduced to 1.0 g/l with stem powders of Moringa tinctroria plant (Vide Graph No. C: 1). With leaves powder of Tridox procumbens, the optimum sorbent dosage has been found to be 1.0 g/l while with its stem powders, it has been reduced to 0.75 g/l (Vide Graph No.C:2). With the Ficus religiosa plant, the optimum dosage has been found to be 1.5 g/l for leaves powder while it is 1.0 g/l with its bark powder (Vide Graph No. C: 2).

6. Interfering Ions: Fivefold excesses of common anions, as given in Table No.1, have not effected the extraction of Methylene Blue from waste waters but Cations like Ca^{2+}, Mg^{2+} and Cu^{2+} have shown interference to some extent; but Fe^{2+} and Zn^{2+} ions synergistically maintained the maximum extraction.

Discussions:

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 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 classical elemental chemical analysis before and after the sorption of the Methylene Blue species on the bio-sorbent surface. It is beyond the aims of this work. However the sorption characteristics may be accounted from the nature of the functional groups present in the plant materials.

The surface of the sorbents derived from plant materials, has potential –OH groups and their dissociation is pH sensitive. At high pH values, the dissociation of –OH groups impart negative charge to the surface and thereby a thrust for cations prevails on the surface. But as the pH decreases, the -OH groups dissociation is less favored and are even protinated, endowing positive charge to the surface which manifests in the thrust for anions at the surface at low pHs.

Methylene Blue being a cation, has natural affinity towards the sorbent surface as pH increases due to the cationic thrust prevailing on the surface of the sorbent. This results in the progressive increase in the % of extraction with the increase in pH value. The maximum extraction is found at pH: above 8.

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 the adsorbent and thus resulting in decrease in capability of the adsorbent.

The observations made with respect to the interfering ions are interesting to note. Anions have not interfered with the extraction of the Methylene Blue at the optimum conditions of extraction as cited in the Table 1 but some cations have marginal interference. This is excepted because the negatively charged surface at the high pH values show less affinity towards anions. The cations like Ca^{2+}, Mg^{2} and Cu^{2+}competes with methylene blue for sorption sites on the sorbents resulting inference. But this is not found in the case of Zn^{2+} and Fe^{2+} because the Zn^{2+} ion forms negatively charged zincate at the high pH resulting no affinity towards the sorbent while Fe^{2+} gets precipitated as ferrous hydroxide at high pH and thus resulting precipitate also adsorbs or traps the methylene dye effecting the complete removal of Methylene Blue dye from the samples.

4: Applications

The Applicability of the methodologies developed in this work have been tested with respects to the real samples of diverse nature, collected from the sewages/effluents of dyeing industries which are fed with varying quantities of the dye: Methylene Blue. **The results have been presented in the Table No: 2**.

It is found that the sorbents developed in this work are successful in removing Methylene Blue at optimum conditions of pH, equilibration time and sorbent dosage as cited in the Table No.2. Percentage of removal of Methylene Blue is found to be between: *92.5% to 95.0%* with leaves powder of *Phyllanthus Niruri* and *90.5% to 95.6%* with *its stem powders*; *93.3% to 97.0 %* with leaves powder of *Moringa Tinctoria* and *92.0% to 97.0%* with *its stems powder*; 86.9*% to 92.0%* with the leaves powders of *Tridox Procumbens* and *91.6% to 95.0%* with *its stems powder*; and 91.9% to 94.0% with leaves powders of Ficus religiosa and *90.0% to 97.9%%* with its stems powder.

5: Conclussions

1. Sorbents derived from plant materials of ***Phyllanthus Neruri, Tridox Procumbens, Moringa Tinctoria and Ficus religiosa*** have been found to have *strong affinity towards Methylene Blue at pH: 8 and 10.*
2. Different physicochemical parameters such as pH, sorbent concentration and time of equilibration for the maximum removal of *Methylene Blue from waste waters have been optimized using simulated waste waters.*
3. The optimum concentration of sorbent and time of equilibration needed for the maximum removal of *Methylene Blue* is less for the leaves powders than the respective plants stems/barks powders as sorbents.
4. Successful methodologies have been established for the removal of substantial amounts of Methylene Blue dye from waste waters.
5. *Fivefold excess* of common anions ions present in natural waters, have not interfered the extractability of Methylene Blue at optimum extraction conditions. *Cation like Ca^{2+}, Mg^{2} and Cu^{2+}* have shown some interference but *Fe^{2+} and Zn^{2+}* have synergistically maintained the maximum extraction of the dye.
6. The procedures have been found to be remarkably successful in removing the Methylene Blue from industrial effluents as detailed in Table No: 2.

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