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METHYL RED DYE REMOVAL USING NEW BIO-SORBENTS DERIVED FROM *HYACINTH AND TINOSPORA CORDIFOLIA* PLANTS FROM WASTE WATERS

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ABSTRACT

The use of eco-friendly, highly efficient, locally available, and low-cost adsorbents have been investigated for removing dyes from waste water and regarded as an ideal alternative to the current expensive methods. Adsorption of methyl red from aqueous solution using dried *Hyacinth* and *Tinospora Cordifolia* is the objective of this study. It was focusing on the effect of decolourisation due to dosage of adsorbent, initial concentration of solution, pH, contact time and the equilibrium of adsorption was modelled by different parameters. Prime pH value for dye adsorption was found to be 4.In the removal of the dye than raw bio-materials, ashes of the bio-materials are more effective. Percentage of extraction is effected in presence fivefold excess of anions. Trivalent anion, divalent, monovalent is the order of the interference. Co-cations have showed less interference. The developed methodologies are enact to industrial samples.

Keywords: Methyl Red (MR), pollution control, Bio-adsorbents, adsorption isotherm, Kinetics, equilibrium models.

INTRODUCTION

Azo, vat, nitro, indigo etc., are some of the types of synthetic dyes which are popularly used for different purposes in printing, paper, textile industry and pulp manufacturing.[1-3]Effluent discharged from the textile industries has variable characteristics in terms of organic and inorganic chemical contents, dissolved oxygen, pH, etc. Due to durability of the dyes in wastewater, dye effluent pollution is caused.[4]Coagulation followed by biological treatment, pH neutralization are utilized by existing effluent treatment procedures. Instead from effluents they are unable to remove recalcitrant dyes completely. This is because of the resistance of dyes to degradation, stability and colour fastness.[5]

A considerable amount of waste water is generated having strong colour, heavy metals, a large amount of suspended solids, sulphides, a highly fluctuating pH salts, chlorine, temperature and COD concentration.[6]Untreated textile wastewater disposal pretends to be a high threat to the environment. It captures a share of 15-20 % of total wastewater in the country.[7]As the synthetic dyes are not biodegradable, conventional methods based on biodegradation is not effective in the controlling of the dye pollution.[8,9] The popular techniques such as ion-exchange, Electro-kinetic coagulation, electrochemical oxidation, membrane filtration, and photo-catalytic degradation process[10-16] are expensive and are not applicable for large scale treatments. We noticed affinity of some dyes towards *Hyacinth* (HY) and *Tinospora Cordifolia* (TC) plants, while probing the biomaterials of different plants for their ability to control dye pollution. The physical methods transfer the pollutants from one medium to another are merely non-destructive thus giving secondary treatment.[17]Due to high dosage and production of a large quantity of sludge chemical methods are not economically viable.[18–20]Thepresent paper reports the findings of degradation of Methyl Red using the HY and TC plants.

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By varying pH, initial concentration of the Methyl red dye contact time, co-ions, temperature and adsorbent dose, the optimization of extraction conditions such as sorption nature of the active bio-sorbents towards Methyl red dye has been studied for the effective removal of Methyl Red from polluted waters. A comparative study has been made in the adsorption processes with Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (D–R) isotherms and dynamics of adsorption have been studied using Weber and Morris intra particle diffusion, pseudo first-order, pseudo second-order, Bangham's pore diffusion and Elovich equations. The methodologies developed using biomaterials derived from the leaves and barks of HY and TC have been applied to the removal of MR from polluted waste waters.

EXPERIMENTAL

Chemicals

Analytical grade chemicals were used.

Stock solution of Methyl Red

By dissolving a requisite amount of A.R. grade Methyl Red dye in double distilled water, 100 ppm of Methyl Red solution was prepared. The solution was suitably diluted based on the requirement.

Preparation of Adsorbents

During the study of plant materials for their sorption abilities apropos the Methyl Red, it was perceived that the adsorbents derived from leaves and stems of HY and TC have shown kinship towards the Methyl red.


Hyacinth Tinospora Cordifolia

Fig.-1: Flora Plants showing affinity towards Methyl Red

Adsorption Experiment

The extraction procedure of Batch system was adopted.[21-23]Circumspect weighted quantities of permeable were taken into formerly washed 1 lit/500 mL stopper bottles containing500 mL/250 mL of Methyl red dye solution of foreordained concentrations. The various primary pH values of the moratorium were adjusted with dil. HCl or dil. NaOH solution using pH meter. The samples were joggled vigorously in mechanical shakers and were allowed to be in equipoise for the desired time. After the equipoise period, an aliquot of the sample was taken for the determination of Methyl Red dye using Spectrophotometric method. The dye has λ_{max} at 464.9 nm and obeys Beers-Lambert's law at low concentrations. The Optical Density (O.D) computations were made using UV-Visible Spectrophotometer (Systronics make) at the said λ_{max}. The retrieved O.D value for strange solution was referred to standard graphs (drawn between O.D and concentration) prepared with familiar concentrations of Methyl Red dye by incorporating Least Squares method.

The sorption features of the permeable were studied with respect to various physicochemical attributes. At a fixed sorbent permeable, with respect to time of equilibration at various pH values the percentage removal of Methyl Red dye from simulated water samples was studied. Graphs A: 1-8 and B: 1-2 shows the results obtained.

For a particular sorbent at prime pH and equilibration times, the minimum dosage needed for the maximum removal of the Methyl Red Dye, extraction investigations were made by investigating the percentage of extraction with respect to the sorbent dosage. Graphs C: 1-4, shows the results obtained.

Methyl Red dye analysis

The percentage removal of Methyl red and amount adsorbed (in mg/g) were calculated using the following equations:

$$\% \text{ of Removal } (\%R) = \frac{Ci-Ce}{Ci} \times 100 \quad (1)$$

$$\text{Amount adsorbed } (qe) = \frac{Ci-Ce}{m} \times V \quad (2)$$

Where, Ci = Initial concentration of the Methyl Red (MR) solution g/L

Ce = Equilibrium concentration of the Methyl Red (MR) solution in mg/L

m = mass of the adsorbent in grams;

V = Volume of Methyl Red (MR) test solution in liters

For different physical and chemical characteristics such as agitation time, adsorbent dosage, pH of the Methyl Red solution, particle size, initial concentration of Methyl Red solution, temperature and in presence of ions, the same procedure has been employed.

Effect of other Co-Ions (Interfering Ions)

For the study of the common ions present in natural waters, the following interfering ions are selected viz. Chloride, Carbonate, Sulphate, Nitrate, Phosphate, Calcium (II), Zinc (II),Copper (II), Magnesium (II) and Iron (II). Methyl Red dye and the co-ions synthetic mixtures are so prepared that the concentration of the foreign ion was maintained at fivefold excess than the dye concentrations. In stopper bottles 500mL of these solutions are taken and then promising adsorbents (as decided by the Graphs A and B) in correctly weighted prime quantities are added. With dil. HCl or dil. NaOH, prime pH was adjusted using pH meter. The samples are joggled in shaking machines for required prime periods and then few portions of the samples are taken out, filtered and analyzed for Methyl Red dye. From the data obtained, percentage of extraction was calculated.

RESULTS AND DISCUSSION

With respect to various physicochemical parameters the sorption characteristics of the bio-adsorbents were studied. The results are presented in the Graphs. A: 1-8, B: 1-2, C: 1-4; Isotherm curves 1(a)-1(h), 2(a)-2(h), 3(a)-3(h), 4(a)-4(h); kinetic parameters graphs 5(a)-5(h), 6(a)-6 (h), 7(a)-7(h), 8(a)-8(h), 9(a)-9 (h), adsorption temperature graphs 10(a)-10(h).

Time of equilibration

For a fixed adsorbent at a fixed pH and after certain duration the following observations are significant, percentage of extractability increases with time, the extractability remains static, i.e. an equilibrium state has been reached (Graphs: A: 1-8). During the steady state, rate of adsorption and the rate of desorption are equal. For plant materials of HY percentage of extraction of Methyl Red dye at pH : 4 has been found to be 19.0% at 15min,27.0% at 30 min , 31.0% at 45 min , 40.0% at 60 min, 47.0% at 75min, 60.0% at 90min, 68.0% at 105min or above for leaves powders (Graphs. A: 1);20.0% at 15 min,25.0% at 30 min, 30.0% at 45 min 41.0% at 60min,58.0 % at 75min,74.0% at 90min and above for leaves ashes (Graphs. A: 2);19.0% at 15 min, 28.0% at 30 min, 39.0% at 45min,47.0% at60min,53.0% at75 min,64.0% at 90 min,70.0%at 105min,75.0% at 125 min and above for stem powder (Graphs. A: 3); and 20.0% at 15 min, 30.0% at 30 min 42.0% at 45 min,54.0% at 60 min,61.0% at 75 min,69.0% at 90 min,80.0% at 105 min and above for the ashes of stem (Graphs. A: 4).

Similarly the bio-materials of TC the % of extraction of the dye at pH:4 has been found to be 18.0 % at 15 min,26.0 % at 30 min, 37.0 % at 45 min, 42.0 % at 60 min, 50.0 % at 75 min, 55.0 % at 90 min 60.0 % at 105 min or above for leaves powders (Graphs. A: 5); 21.0 % at 15 min, 30.0 % at 30 min,40.0 % at 45 min, 50.0 % at 60 min,60.0 % at 75 min, 65.0 % at 90 min,73.0 % at 105 min or above (Graphs. A: 6) for leaves ashes;21.0 % at 15 min,31.0 % at 30 min,40.0 % at 45min, 45.0 % at60 min, 50.0 % at 75 min, 56.0 % at 90 min,64.0 % at 105 min, and above for stem powder (Graphs.A:7); and 30.0 % at 15 min, 35.0 % at 30 min, 42.0 % at 45 min, 50.0 % at 60 min, 56.0 % at 75 min, 73 % at 90 min and above for the ashes of stem (Graphs. A: 8).

pH sensitivity

The percentage of extraction referred to be pH sensitive. In the pH: 4 and above the percentage removal of the Methyl Red is more and below this pH range, the percentage removal has been decreasing (Graphs. B: 1 and 2).

Considering the extract of leaves powder of HY, the maximum extractability, has been found to be 0.0 % at pH: 0 (1.0 N HCl) 52.0 % at pH:2, 68.0 % at pH:4, 49.0 % at pH:6,40.0 % at pH:8,35.0 % at pH:10 compared with the ashes of leaves of HY, the maximum % removal of the dye has been found to be: 0.0 % at pH:0 (1.0 N HCl), 60.0 % at pH: 2, 74.0 % at pH: 4, 56.0 % at pH: 6, 50.0 % at pH: 8, 40.0 % at pH: 10, (Graphs.B:1). With the stem powder of *Hyacinth*, the % of extraction has been found to be 0.0 %, 60.0 %, 75.0 %, 55.0 %, 40.0 %, 35.0 % at pH's:0(1.0HCl),2,4,6,8 and10 respectively.The percentage of extraction has been found to be 0.0%, 65.0 %, 80.0 %, 60.0 %, 45.0 % and,40.0 % respectively with stem ashes, for the same sequence of pHs (Graphs: B:1).

The plant materials of TC consequently, the maximum percentage removal at pH: 0 (1.0 N HCl), 2,4,6,8 and 10 has been found to be 50.0 %, 60.0 %, 55.0 %, 40.0 % and 30.0 % respectively for leaves powder;59.0 %, 73.0 %, 64.0 %, 50.0 % and 40.0 % for leaves ash, 55.0 %, 64.0 %, 50.0 %, 45.0 % and 33.0 % for stem powder; 60.0 %, 73.0 %, 58.0 %, 47.0 % and 35.0 % for stem ash (Graphs.B:2).

Adsorbent Dosage

When percentage eviction is reviewed with respect to adsorbent dosage at fixed prime pH: 4 and at prime equilibration times, the graphs rise up to certain dosage and from then onwards plateaus are obtained (Graphs. C:1-4). The prime sorbent dosage has been to be less for ashes than the raw plant materials.

In addition to the sorbent pertaining to HY plant, the prime adsorbent congregation has been found to be: 2.5 gm/L for leaves and 2.0 gm/L for their ashes, 2.5 gm/L for stem powders and 2.0 gm/L for their ashes. For TC plant, the prime sorbent dosage leads to be: 2.0 gm/L for leaves and 1.75 gm/L for their ashes, 2.0 gm/L for stem powders and 1.5 gm/L for their ashes. Graphs C: 1 and 4 shows the results.

With the respective raw plant materials, the prime time of agitation is found to be less for ashes. For the stems powder of HY plant, the prime time is found to be 125 min but 105 min is sufficient with their ashes as sorbents. With TC leaves powder as adsorbent, the prime agitation time has been found to be 105 min but with their ashes, it has been reduced to 90 min, with stems powder of the same plant, prime equilibration is found to be 125 min while 90 min of agitation is enough with ashes stems (Graphs. A: 1-8).

The following observations were accounted

The sorbents retrieved from plant materials may have some functional groups like -OH/COOH and their dissociation is pH dependent. This emphasizes poor anion exchange ability at low pH: 3 values and poor cation exchange ability at high pH values as per the equilibrations: The acid dissociation constant of Methyl Red dye is pK: 4.95 and the dye will be changing from quinonoid form to benzenoid form in the pH range 4.4-6.2 yielding anion on dissociation. Moreover, the dye is in anionic form and surface is positively charged, adsorption of the dye is more. However, the Vander Waals synergy and Hydrogen bonding formations between surface and dye may abound but these forces will be nullified because of the presence of aquated hydronium ions in the contacting solution of the sorbent surface.

It is observed that around pH: 4 only the dye shows affinity towards the sorbents. Decrease in sorption may be caused due to Increasing or decreasing of the pH (other than prime pH: 4), of the equilibrating solution. Initially, the rate of adsorption is found to be more but reduces with time and reaches study state after certain time. Initially many active sites are available for the sorption process to occur and they are progressively utilised with time and hence, rate of adsorption is reduced. There will not be active sites on the sorbent surface for the adsorption process to take place after certain time as saturation state is reached and during this stage there will not be adsorption further.

Adsorption Isotherms

Some of the popular adsorption isotherm models such as Freundlich[24], Langmuir[25], Temkin[26] and Dubinin-Radushkevich[27] isotherms have been adopted to evaluate the relation between the Methyl Red concentrations remaining in the bulk solution to the amount of Methyl Red adsorbed at the solution interface at a constant temperature.

Linear form of Freundlich equation is-

$$\log (q_e) = \log k_f + \frac{1}{n} \log C_e \quad (3)$$

Linear form of Langmuir equation is-

$$C_e/q_e) = (a_L/k_L)C_e + 1/k_L \quad (4)$$

Hall *et al*[28] proposed that the nature of the adsorption process is not rewarding ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) and irreversible ($R_L = 0$) and the significant parameter of the Langmuir isotherm model can be defined by the dimensionless separation factor, $R_L = 1/\ (1 + a_L C_i)$. The plots which are linear of these two adsorption isotherms were as shown in graphs 1(a)-2(h) (provided in SI file) and isothermal constants along with the correlation coefficient values were presented in Table-1 and 2. As the correlation coefficient (R^2-values) is close to unity, the applicability of these two adsorption isotherms confirmed the heterogeneous surface of the adsorbent and the monolayer coverage of Methyl Red on the bio-sorbents. The applicability of the isotherm equations is compared from the correlation coefficient (R^2) of these four Isotherm models, the correlation coefficient value of leaves and Bark powders and Ashes of HY and TC for the high correlation coefficient for Freundlich isotherm. (R^2=0.997) value, Langmuir isotherm (R^2=0.976) and dimensionless separation factor (R_L=0.0791), value which has been found to be fraction in the range of 0-1, indicate the favourability of the Langmuir isotherm than the Freundlich isotherm.

Linear form of Temkin equation is-

$$sq_e = B\ln Ce + B\ln A \text{ where } RT/b = B \quad (5)$$

Linear form of Dubinin-Radushkevich equation is-

$$\ln q_e = -\beta\varepsilon^2 + \ln qm \quad (6)$$

Where, $\varepsilon = RT \ln(1+1/C_e)$

Table-1: Freundlich Isotherm

S. No.	Name of the sorbent	Slope	Intercept	R^2
1a	LPOH	0.393	0.849	0.996
1b	LAOH	0.361	1.023	0.994
1c	SPOH	0.380	1.041	0.990
1d	SPOH	0.323	1.292	0.967
1e	LPOTC	0.356	0.625	0.964
1f	LAOTC	0.410	0.801	0.995
1g	BPOTC	0.392	0.886	0.997
1h	BAOTC	0.370	1.019	0.989

Table-2: Langmuir Isotherm

S. No.	Name of the sorbent	R^2	Slope	Intercept	R_L
2a	LPOH	0.976	0.034	0.156	0.0439
2b	LAOH	0.943	0.025	0.108	0.0414

2c	SPOH	0.976	0.024	0.089	0.0358
2d	SPOH	0.963	0.018	0.046	0.0250
2e	LPOTC	0.946	0.051	0.438	0.0791
2f	LAOTC	0.969	0.038	0.159	0.0402
2g	BPOTC	0.960	0.031	0.148	0.0456
2h	BAOTC	0.968	0.025	0.096	0.0370

Graphs 3(a)-4(h)(provided in SI file) show the linear plots of these two adsorption isotherms and isothermal constants along with the correlation coefficient values were presented in Table-3 and 4.The correlation coefficients (R^2-values) are close to unity. The Temkin heat of sorption, (B= 6.717 jol/mol) was calculated from the slope of the Temkin linear plot[29-30], and the Dubinin- Radushkevich mean free energy E =$\sqrt{1/2\beta}$, [31] was found to be E=2.3570 KJ/mol calculated for the leaves and bark powder and ashes of HY and TC. As the E < 8 kJ/mol, representing 'physical adsorption[32] upholding the chemical adsorptions and ion exchange etc. The "physical adsorption'' is also referred as nonspecific adsorption which occurs as a result of long range weak Vander Waals forces between Methyl Red and adsorbent. According to Atkins[33], the characteristics for "physical absorption' is the mean free energy (E) and also heats of sorption (B) values lower than 20kJ/mol.

Table-3: Temkin Isotherm

S. No.	Name of the sorbent	B	Slope (B)	Intercept	R^2
1a	LPOH	51.34	4.858	7.853	0.951
1b	LAOH	43.64	5715	12.76	0.879
1c	SPOH	40.57	6.150	13.45	0.904
1d	SPOH	34.13	6.717	24.13	0.842
1e	LPOTC	90.73	2.749	4.487	0.836
1f	LAOTC	58.44	4.268	7.557	0.936
1g	BPOTC	50.43	4.946	9.032	0.900
1h	BAOTC	43.10	5.787	12.92	0.911

Table-4: Dubinin-Radushkevich

S. No.	Name of the sorbent	E	Slope (B)	Intercept	R^2
1a	LPOH	7.0711	$1x10^{-8}$	1.584	0.715
1b	LAOH	3.1623	$5x10^{-8}$	0.830	0.659
1c	SPOH	3.5355	$4x10^{-8}$	1.842	0.628
1d	SPOH	5.0000	$2x10^{-8}$	2.158	0.605
1e	LPOTC	2.6726	$7x10^{-8}$	1.078	0.568
1f	LAOTC	2.3570	$9x10^{-8}$	1.469	0.603
1g	BPOTC	2.6726	$7x10^{-8}$	1.596	0.648
1h	BAOTC	3.1623	$5x10^{-8}$	1.827	0.657

Adsorption Kinetics

With pseudo first-order model [34, 35] pseudo second-order model [35,36], Weber and Morris intra particle diffusion model [37], Bangham's pore diffusion model [38] and Elovich equations [39,40] the rate and kinetics of adsorption of methyl red on to the bio-sorbents derived from HY and TC was studied.

The pseudo first-order equation is-

$$\log (qe - qt) = \log q_e - \frac{k1}{2.303} \times t \tag{7}$$

The pseudo second-order equation is-

$$t/qt = \frac{1}{k2qe2} + (1/qe)\ t \tag{8}$$

Weber and Morris intra particle diffusion equation is-

$q_t = k_{ip}t^{1/2} + c$ (9)

Bangham's pore diffusion equation is-

$\log [\log (C_i/C_i - q_t m)] = \log (ko/2.303V) + \alpha \log (t)$ (10)

Elovich equation is-

$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t)$ (11)

The linear graphs of all these five kinetic models were as shown in graphs 5(a)-9(h) (provided in SI file) and rate constants along with the correlation coefficient values were presented in Tables-5 and 9. The usage of the kinetic equations is compared from the correlation coefficient (R^2). Of these five kinetic models, the correlation coefficient value of leaves and bark powders and ashes of HY and TC for the Weber and Morris ($R^2 = 0.997$), Bangham's pore diffusion model ($R^2 = 0.994$) pseudo first-order model ($R^2 = 0.978$), pseudo second-order model (R^2=0.987) and Elovich model (R^2=0.985).

Effect of Temperature

By conducting the extraction experiments at different temperatures 298, 308, 318 and 328 K the effect of solution temperature on the % removal of Methyl red was studied at prime conditions of extraction: pH: 4.0; contact time: 90 min; sorbent dosage: 3.0 mg/L; concentration of methyl red dye solution: 100 mg/L; particles size: 45 μ mesh. The results obtained were plotted as $\ln(K_d)$ Vs 1/T. Thermodynamic parameters of the adsorption process such as change in free energy (ΔG) kJ/mole, change in enthalpy (ΔH) kJ/mole and change in entropy (ΔS) KJ/mole were calculated at different temperatures by using the equations:[41-43]

$\Delta G = -RT \ln(K_d)$ (12)

$\mathrm{Ln}(Kd) = \Delta S/R - \Delta H/RT$ (13)

$K_d = q_e/C_e$ and $\Delta G = \Delta H - T\Delta S$ (14)

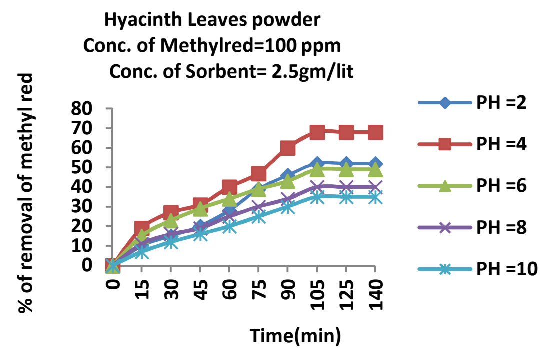
Where, K_d is the distribution coefficient for the adsorption, q_e is the amount of methyl red adsorbed on the adsorbent per liter of solution at equilibrium, C_e is the equilibrium concentration of methyl red dye solution is the absolute temperature in Kelvin, R is the gas constant. ΔG is the change in free energy, ΔH is the change in enthalpy, ΔS is the change in entropy.

Table-5: Pseudo first Order

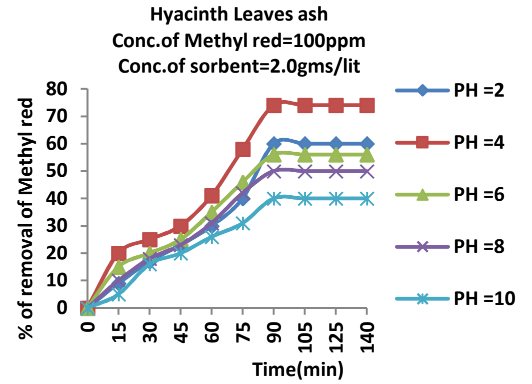
S. No.	Name of the sorbent	K_1	Slope (B)	Intercept	R^2
1a	LPOH	0.0207	0.009	1.518	0.847
1b	LAOH	0.0184	0.008	1.625	0.829
1c	SPOH	0.023	0.010	1.674	0.894
1d	SPOH	0.0207	0.009	1.800	0.974
1e	LPOTC	0.0276	0.012	1.333	0.956
1f	LAOTC	0.0253	0.011	1.475	0.964
1g	BPOTC	0.0209	0.009	1.399	0.978
1h	BAOTC	0.0138	0.006	1.465	0.973

Table-6: Pseudo Second Order

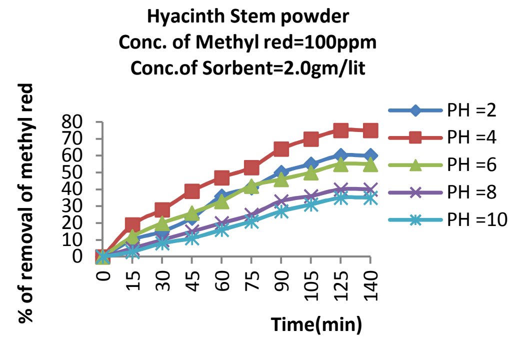
S. No.	Name of the sorbent	K_2	Slope	Intercept	R^2
1a	LPOH	0.0003	0.026	1.960	0.840
1b	LAOH	0.0002	0.018	1.672	0.503
1c	SPOH	0.0004	0.021	1.031	0.875
1d	SPOH	0.0009	0.01	1.091	0.925
1e	LPOTC	0.0006	0.040	2.497	0.961
1f	LAOTC	0.00025	0.023	2.084	0.916
1g	BPOTC	0.00057	0.029	1.452	0.987
1h	BAOTC	0.00094	0.027	0.774	0.949



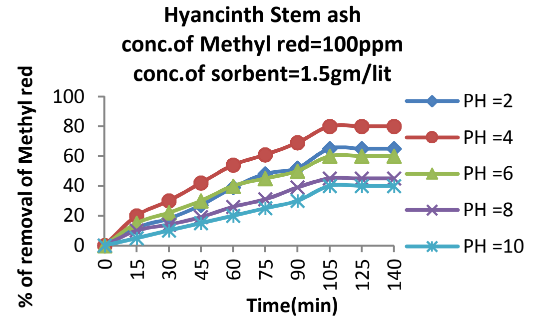
Equalibration Time Vs% of removal of methyl red
Graph No:A-1



Equalibration Time Vs % of removal of Methyl red
Graph No:A -2



Equalibration TimeVs % removal of methyl red
Graph No:A--3



Equalibration Time Vs % of removal of Methyl red
Graph No:A -4

Table-7: Bangham's pore diffusion

S. No.	Name of the sorbent	K_0	Slope	Intercept	R^2
1a	LPOH	0.3189	0.762	-1.977	0.935
1b	LAOH	0.3170	0.770	-1.983	0.851
1c	SPOH	0.0278	0.824	-1.985	0.960
1d	SPOH	0.2598	0.956	-2.182	0.990
1e	LPOTC	0.3095	0.786	-2.007	0.990
1f	LAOTC	0.3033	0.852	-2.027	0.981
1g	BPOTC	0.3829	0.683	-1.794	0.994
1h	BAOTC	0.5423	0.515	-1.446	0.942

Table-8: Weber and Morris

S. No.	Name of the sorbent	Slope	Intercept	R^2
1a	LPOH	2.755	-4.329	0.937
1b	LAOH	3.720	-6.759	0.860
1c	SPOH	3.739	-4.313	0.965
1d	SPOH	5.993	-11.23	0.992
1e	LPOTC	1.928	-2.623	0.993
1f	LAOTC	2.732	-4.324	0.988
1g	BPOTC	2.458	-0.991	0.997
1h	BAOTC	3.569	-1.123	0.904

Table-9: Elovich

S. No.	Name of the sorbent	Slope	Intercept	R^2
1a	LPOH	8.334	-16.77	0.868
1b	LAOH	10.48	-21.02	0.776
1c	SPOH	12.14	-23.96	0.948
1d	SPOH	18.51	-39.75	0.958
1e	LPOTC	5.973	-11.86	0.965
1f	LAOTC	8.411	-17.22	0.949
1g	BPOTC	7.682	-13.02	0.985
1h	BAOTC	10.71	-16.91	0.825

The values of ΔH and ΔS were calculated from the slope and intercept of a plot between ln (K_d) and 1/T and ΔG values were calculated from the equation ΔG = ΔH-TΔS and tabulated [44-45.]
With increase in temperature from 298 to 328 K 25 to 55 °C, the maximum extraction of methyl red takes place at 328 K. The thickness of outer surface of the adsorbent decreases and kinetic energy of the methyl red increases as the temperature increases. Therefore, the rate of diffusion of methyl red increases across the external boundary layer and internal pores of the adsorbent.
From Table-10 it can be inferred that, the values of ΔH are positive, indicating the physical sorption and endothermic nature of adsorption [46]. The R^2 values close to one also indicates that adsorption process is endothermic nature. The +ve values of ΔS represent the increased disorder and randomness at the solid solution interface of methyl red dye with the adsorbent [47]. The -ve values of ΔG indicate the spontaneous nature of adsorption process i.e. the adsorptive forces are strong enough to overcome the potential barrier[48.]

Table-10: Effect of temperature: parameter (temp.(K))

S. No.	Name of the sorbent	ΔH kJ/mol)	ΔS (J/mol/K)	ΔG (kJ/mol)	R^2
1a	LPOH	7.51419	0.021034	0.6149	0.950
1b	LAOH	8.7130	0.028957	-0.7851	0.985
1c	SPOH	8.9624	0.030088	-0.9066	0.957
1d	SPOH	9.9019	0.037687	-2.4596	0.984
1e	LPOTC	7.4709	0.015289	2.4560	0.988
1f	LAOTC	8.1510	0.023628	0.4008	0.966
1g	BPOTC	7.6564	0.020045	1.0816	0.988
1h	BAOTC	8.2483	0.027140	-0.6526	0.989

LPOH = Leaves Powder of Hyacinth
LAOH = Leaves Ash of Hyacinth
SPOH= Bark powder of Hyacinth
SAOH = Bark ash of Hyacinth
LPOTC = Leaves Powder of Tinospora Cordifolia
LAOTC = Leaves ash of Tinospora Cordifolia
BPOTC = Bark powder of Tinospora Cordifolia
BAOTC = Bark ash of Tinospora Cordifolia

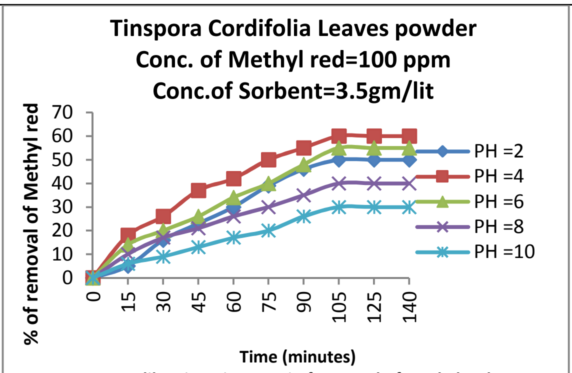
Effect of interfering ions

The effect of the inclusion of fivefold excess of co-ions on the extraction of the methyl red dye from simulated waters, is presented in the Table-11. It can be stated that bivalent anions likeCO_3^{2-} and SO_4^{2-} and PO_4^{3-} 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 fluctuating from 70.5 % to 86.0 % with the eight sorbents developed in this work but the extraction has been seriously affected to 15.0 % to 29.0 % in presence of fivefold excess of $SO4^{2-}$, 11.0 to 22.0 % 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-}.

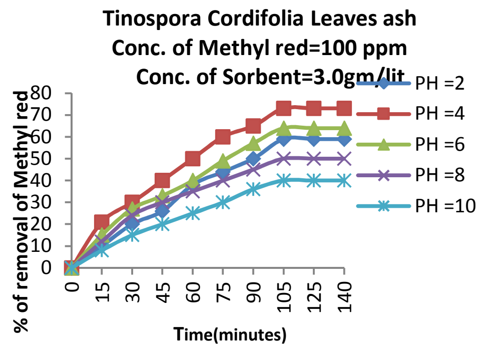
The co-cations studied viz., Ca^{2+}, Mg^{2+}, Fe^{2+}, Zn^{2+} and Cu^{2+} have less interfered with the % of extraction of the dye. 70.5 to 86.0 % extraction of the dye in the absence of the co-ions, has been reduced to 53.0-67.5 % in presence fivefold excess of Ca^{2+}, 47.8-56.0 % for Cu^{2+}, 54.0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

Applications of the Developed Bio-sorbents

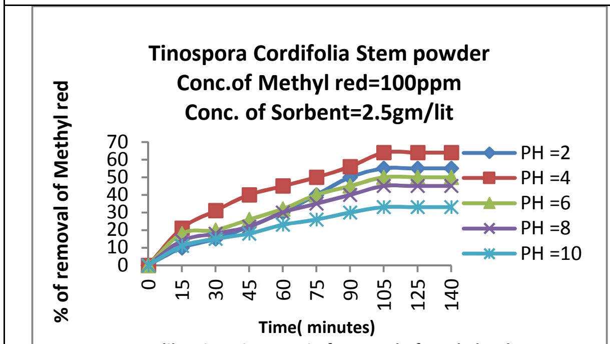
The developed methodologies have been applied for samples collected from the effluents of Dyeing industries, sewages which are fed with varying quantities of the Methyl Red dye. Table-12 shows the results. It is shown from the data that 80-90 % Methyl Red dye can be removed from the waste waters.



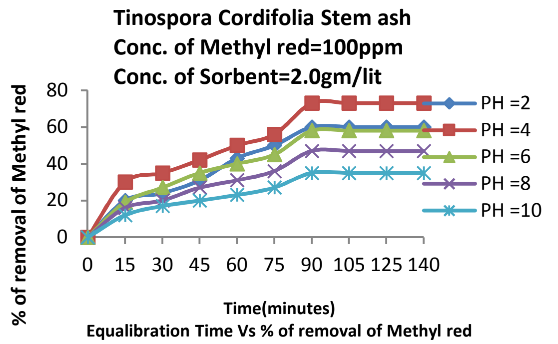
Equalibration Time Vs % of removal of Methyl red
Graph No:A-5



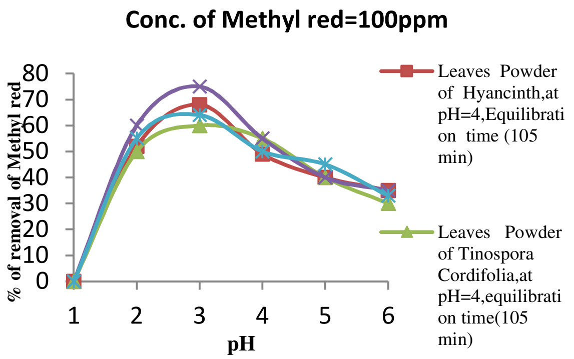
Equalibration Time Vs % of removal of Methyl red
Graph No:A --6



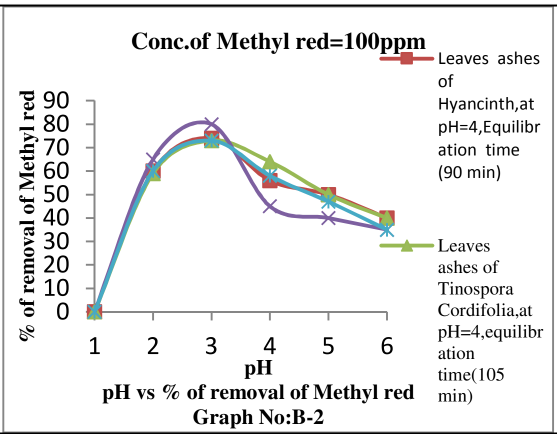
Equalibration Time Vs % of removal of Methyl red
Graph No:A -7



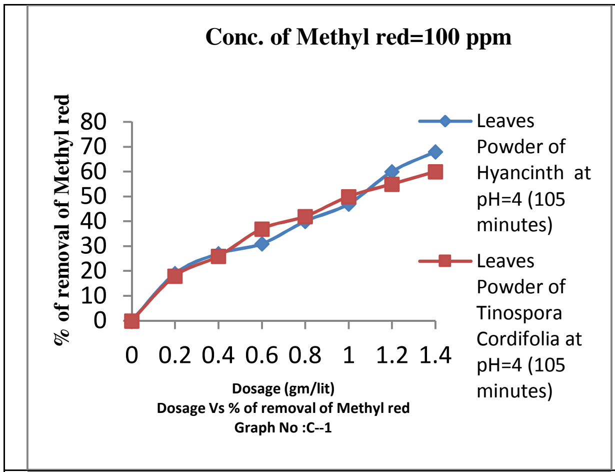
Equalibration Time Vs % of removal of Methyl red
Graph No: A - 8



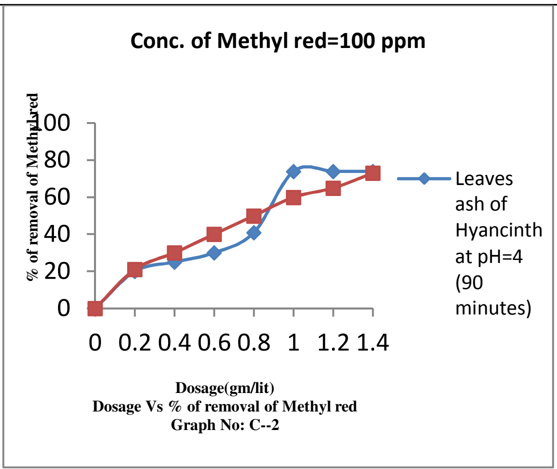
pH vs % of removal of methyl red
Graph No: B-1



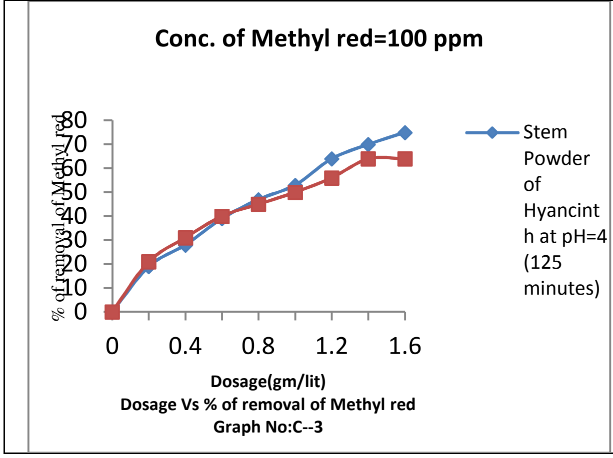
pH vs % of removal of Methyl red
Graph No:B-2



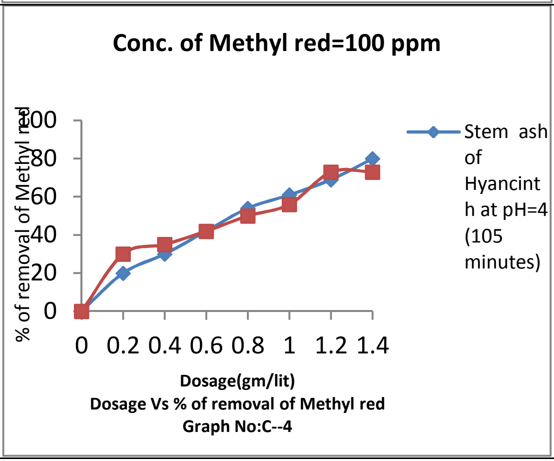
Dosage Vs % of removal of Methyl red
Graph No :C--1



Dosage Vs % of removal of Methyl red
Graph No: C--2



Dosage Vs % of removal of Methyl red
Graph No:C--3



Dosage Vs % of removal of Methyl red
Graph No:C--4

Table-11: Effect of interfering Ions on the Extractability of Methyl Red with different Bio-sorbents: 65 to 99 between values

S. No.	Adsorbent and its concentration	Maximum Extractability at prime conditions	% of Extraction of Methyl Red in presence fivefold excess of interfering ions at prime conditions: Conc. of Methyl Red : 100 ppm at pH:4									
			SO_4^{2-}	PO_4^{3-}	Cl^-	CO_3^{2-}	F^-	Fe^{2+}	Ca^{2+}	Mg^{2+}	Cu^{2+}	Zn^{2+}
1	*Leaves Powder of Hyacinth:2.5gms/lit*	68.0%; pH:4, 105 min	79.0	82.1	84.2	87.0	86.0	82.5	67.5	74.0	68.	63.0
2	*leaves Powder of Tinospors Cordifolia:2.0gms/lit*	74.0%; pH:4, 90 min	83.0	89.2	92.0	88.9	91.2	86.6	83.4	66.5	89.4	93.0
3	*Bark Powder of Hyacinth 2.0gms/lit*	75%; pH:4, 125 min	77.0	69.2	87.5	82.1	98.3	77.5	69.1	68.3	77.5	85.5
4	*Bark Powder of Tinospors Cordifolia 2.5gms/lit*	64.0%; pH:4, 105min	92.0	77.5	84.2	87.0	86.0	82.5	67.5	.0	68.0	63.0
5	*leaves Ashes of Hyacinth ;2.0 gms/lit*	74.0% pH:4, 90 min	83.1	84.0	85.0	88.1	92.0	89.5	83.1	80.0	78.5	83.0
6	*leaves Ashes of Tinospors Cordifolia;3.0gms/lit*	73%; pH:4, 105 min	79.2	81.4	85.7	86.5	85.2	81.3	67.1	73.8	67.6	64
7	*Bark Ashes of Hyacinth 1.5 gms/lit*	80.0% pH:4, 105 min	82.6	83.2	84.6	87.2	91.8	88.0	82.4	79.2	77.6	82.1
8	*Bark Ashes of Tinospors Cordifolia 2.0gms/lit*	73.0% pH:4, 90 min	89.5	86.2	86.1	78.5	92.1	98.5	68.3	74.0	68.0	63.0

Table-12: % of Extractability of Methyl Red from effluents with bio-sorbents developed in this work. 80 to 90 between values

Bio-Sorbents	% of extraction of methyl red in diverse samples					
	Sample -1 Fed with 10.0ppm methyl red dye	Sample -2 Fed with 15.0ppm methyl red dye	Sample -3 Fed with 20.0ppm methyl red dye	Sample -4 Fed with 25.0ppm methyl red dye	Sample -5 Fed with 30.0ppm methyl red dye	Sample -6 Fed with 35.0ppm methyl red dye
Powder of *Hyacinth l*eaves:3.0 gms/lit	81.5	90.0	82.3	81.2	85.5	86.3
*Powder of Tinospors Cordifolia leaves:2.0*gms/lit	83.5	91.1	85.5	88.3	87.4	82.1
Powder of Hyacinth Bark 2.5gms/lit	88.1	82.2	85.6	88.3	81.5	83.5
Powder of Tinospors Cordifolia bark 2.0gms/lit	89.1	88.2	85.2	86.4	88.2	85.5
Ashes of Hyacinth leaves;2.5gms/lit	87.3	81.5	85.5	85.4	89.0	85.2
*Ashes of Tinospors Cordifolia*leaves ;1.75gms/lit	88.5	82.3	86.4	81.5	85.3	84.6
*Ashes of Hyacinth Bark 2.0*gms/lit	86.5	88.3	89.0	85.2	83.5	86.5
Ashes of Tinospors Cordifolia bark 1.5gms/lit	86.3	86.5	84.4	88.3	89.5	83.5

CONCLUSION

For the sorption abilities towards Methyl Red dye from polluted waters is due to Bio-adsorbents derived from plant materials of *Hyacinth* and *Tinospors Cordifolia*. Extraction parameters such as sorbent dosage, pH, and time of equilibration have been adaptive for the maximum removal of Methyl Red dye. % removal of the dye is high when the pH of the extraction system is approximately 4. Ashes found to be more effective than respective raw bio-materials. Fivefold excess of di- and trivalent co-anions found to be interfering while the monovalent anions to a less extent. Co-cations have showed less interference.

The four Isotherm models, the correlation coefficient value of leaves and bark powders and ashes of HY and TC for the high correlation coefficient for Freundlich isotherm (R^2=0.9965) value, Langmuir isotherm (R^2=0.9964) and dimensionless separation factor (R_L=0.0901) value which has been found to be fraction in the range of 0-1, indicate the favourability of the Langmuir isotherm than the Freundlich isotherm. The correlation coefficient value of leaves and bark powders and ashes of Hyacinth and TC for the Weber and Morris (R^2 = 0.991), Bangham's pore diffusion model (R^2 = 0.992) pseudo first-order model (R^2 = 0.982), pseudo second-order model (R^2=0.951) and Elovich model (R^2=0.979).It is observed that the pseudo second-order model fits well to the experimental data of the proposed adsorption system. The values of ΔH are +ive, indicating the physical sorption and endothermic nature of adsorption.

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