Dye Removal Using Peat

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The textile industry, a major consumer of water for several of its wet processing operations, is also a major producer of effluent wastewater containing organic surfactants, salts, acids, alkalis, solvents and dyes as some of its main constituents. Dyes, though present in only small amounts are highly detectable and thereby are capable of causing serious problems of an aesthetic nature in the receiving water bodies. In fact, most of the commercially used dyes are resistant to biodegradation,[i] photodegradation* and even oxidizing agents.[3] Unless and otherwise properly treated, these dyes can significantly affect photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to certain forms of aquatic life due to the presence of metals and chlorides in them.[4]

Dyes have also been known to interfere with certain municipal wastewater treatment operations such as ultraviolet disinfection, etc. A major contributor to color in textile wastewater is usually the washing operation after dyeing, during which as much as 50 % of the dye might be exhausted into the effluent.[5]

Given the inadequacy of biological methods for effective dye removal, adsorption has come to stay as one of the popular physical/chemical methods successfully employed for decolorization. The emphasis has of late, however shifted towards low-cost adsorbents which can serve as viable alternatives to the more expensive activated carbon.

The present page is aimed at studying the adsorption capacity of peat-a

Table I: Typical analysis of sphagnum peat.*

Parameter	Value
Classification	Type 1 - between class A & B
pH	4.5-5.7
Salinity	0.3 - 0.8 m mhos/cm
Moisture	40 - 70 %
Bulk density	62.3 - 118.7 kg/m³
Organic matter	90 - 95 %
Total Carbon	44.43 - 45.61 % (w/w)
Total Hydrogen	5.22 % (w/w)
TotalNitrogen	1.01 - 1.32 % (w/w)
Nitrate	118 - 397 mg/L
Dilute acid soluble iron	80 - 250 mg/L
Phosphorus	80 - 250 mg/L
Potassium	650 - 2000 mg/L
Calcium	12580 - 15510 mg/L
Magnesium	4300 - 5550 mg/L
Boron	3 - 10 mg/L
Manganese	95 - 350 mg/L
Total porosity	70 - 85 %
Screen size 9.51mm	% retained: O - 10
Screen size 6.35 mm	% retained: O - 20
Screen size 2.38 mm	% retained: 12 - 32
Screen size 0.50 mm	% retained: 62 - 80
Surface area	57.41 - 108.53 m²/g
Cation exchange capacity	72.6 meq/lOOg

* Source: Premier Peat Ltd., Carrot River, Saskatchewan.
Note: Surface area, total carbon, hydrogen, nitrogen and CEC values were determined at the University of Regina.

Table II: pH conditions for maximum dye removal.

Adsorbent	Dye	IdealpH value
	Basic Blue 9	6
Horticultural peat	Acid Blue 29	2
	Acid Red 91	-
	Disperse Red 1	2

...al-y available low-cost adsorbent in Saskatchewan, Canada for dye removal from wastewaters, with simultaneous comparison of its performance vis-à-vis granular activated carbon (GAC). The ...us here. is upon a commercial vari-e... of peat. i.e. the horticultural peat ...ch is widely used as an organic fer-...er in gardening. Batch and column studies were conducted on a laboratory scale using synthetic dye wastewaters made up from four different commercial grade dyes. The scope included batch ... kinetic / isotherm and subsequent ... studies for certain dye-adsor-b... combinations that showed promise du...ng batch studies. The Langmuir, Freundlich and BET isotherm models were tested for their applicability, and the column data was analyzed using the Thomas equation.
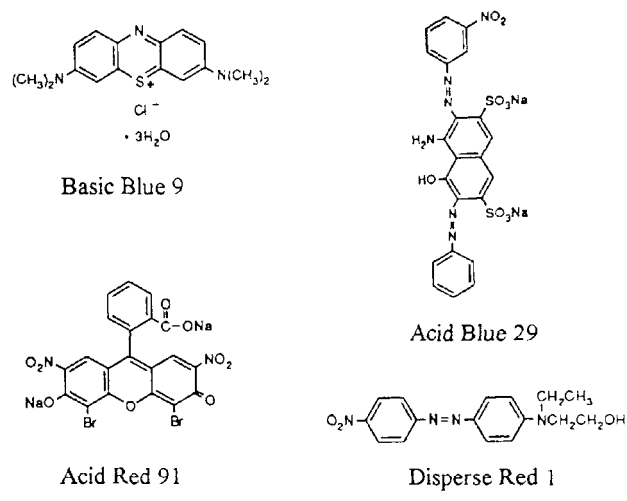
Materials and Methods

Dyes utilized in this study were Basic Blue 9 - a cationic thiazine dye (C.I. 52015 λ_{max} = 660 nm), Acid Blue 29 - an anionic disazo dye (C.I. 20460, λ_{max} = 600 nm), Acid Red 91 - an anionic xan-thene dye (C.I. 45400, λ_{max} = 530 nm) and Disperse Red 1 - a monoazo sol-vent dye (C.I. 11110, λ_{max} = 450 nm), all supplied by Sigma chemical company, St. Louis, MO. USA. Chemical structures for these dyes are shown in Figure 1.

Horticultural peat was supplied by Premier Peat Limited, Carrot River, Saskatchewan and the GAC used in this study (Filtrasorb 400) was supplied by Calgon carbon corporation, Pittsburgh. PA. The characteristics of peat are given in Table I.

Synthetic dye wastewaters were pre-pared by dissolving the different dyes in distilled deionized water at concentra-tions of 50mg/L. The peat moss was ini-tially washed in tap water followed by deionized water and then dried in an oven for 24 hours at 100°C. The dried peat samples were then broken down and screened through an ASTME: 11, #20 sieve prior to their use in experi-ments. All color measurements were made with a Baush & Lomb-Spectronic 21 spectrophotometer operating in the visible range on absorbance mode. Absorbance values were recorded at the wavelength for maximum absor-bance (λ_{max}) corresponding to each dye and each dye solution was initially cali-brated for concentration in terms of absorbance units.

Batch pH studies were conducted by stirring 100mL of each dye solution at 125 rpm with 0.5g of peat for 24 hours over a range of pH values from 2 to 11. IN HCl or IN NaOH was used for pH adjustment. Blanks were run simultane-ously, without any adsorbent to deter-mine the impact of pH change on the dye solutions. Prior to measurement of color, the dye solutions were filtered through a 1.25,um glass fiber filter to remove any suspended matter.

Once the optimum pH was identified, kinetic studies were conducted by shak-ing 0.5g of peat in 100mL of each dye solution at this optimum pH, for increas-ing periods of time, until no more dye was removed and equilibrium was achieved. Isotherm studies were con-ducted by shaking differing quantities of peat varying from 0.1 g to 1 .Og in 1 OOmL of each dye solution for a time period equal to the equilibrium time for that dye. Blank runs with only peat in 1 OOmL

Figure I-Dyes used in the study.[6]

Basic Blue 9

Acid Blue 29

Acid Red 91

Disperse Red 1

of deionized water, were conducted simultaneously at similar conditions to account for any color leached by peat and also any color adsorbed by the glass container.

Column studies were carried out in a glass column with a diameter of 27mm, and a packing volume equal to 200 cm3 The dye flow rate through the column was controlled at 11 mL/min by means of a Masterflex pump. Column effluent samples were collected at frequent intervals and measured for color, until the column achieved breakthrough.

Results and Discussion
pH studies:

Table II summarizes the pH conditions for maximum removal in the case of each dye with peat and Figures 2a & 2b show the removal capacities of peat for each of the dye types at different initial pH conditions. Most dyes are ionic in nature, which upon dissolution release colored dye anions/cations into solution. The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent which in turn is influenced by the solution pH.

Peat surface is essentially negatively charged due to the presence of polar functional groups viz. humic and fulvic acids,[7,8] which are responsible for its high adsorption capacity for cationic (basic) dyes. The maximum affinity for these dye cations can be expected at higher pH values, because of fewer anionic adsorption sites on peat and an increased competition from protons for these active sites, at lower pH values. Although peat exhibited consistently high removals for Basic Blue 9 at all pH values, the maximum dye adsorption was observed at a pH of 6-7, with no significant increase in removals beyond pH 7. This might be because of the decreased positive charges on the dye groups at higher pH values.[9] The observed values also agree well with the results obtained by Viraraghavan and Mihial.[10] The adsorption of anionic dyes is not as effective as cationic dyes as a result of their repulsion by the negatively charged adsorption sites on peat. In any case, at decreased pH values, this repulsion towards anionic dye groups is very much reduced and maximum removal of Acid Blue 29 was observed at pH 2.

The pH studies could not be conducted on Acid Red 91, since the dye behaved as a pH indicator and changed color with changes in pH. In any case,

Figure 2-pH studies on peat (Basic Blue 9).
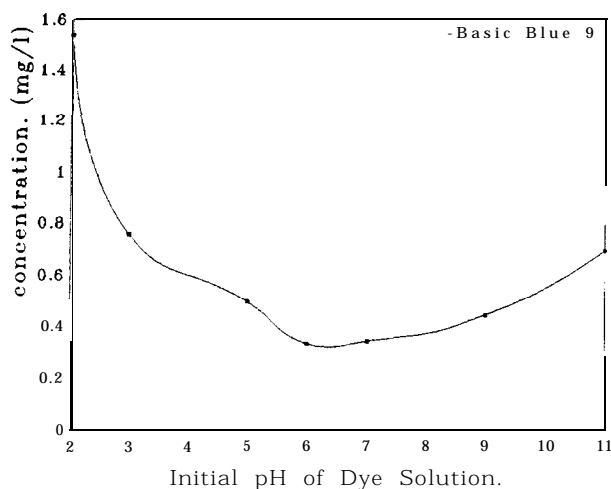
Figure 2b-pH studies on peat (Acid Blue 29 & Disperse Red 1)

the main difference between Acid Red 91 and Acid Blue 29 is the difference in electronegativity due to differing acidifying groups in the dye structure (Figure 1). The acidity in Acid Blue 29 is due to the sulfonic acid group, while it is due to the carbonic acid group in Acid Red 91 as a result of which Acid Red 91 anions are more electronegative than Acid Blue 29 anions. Hence, the removal or nonremoval due to the anionic nature of these dyes is greater in the case of Acid Red compared to Acid Blue.

The low aqueous solubility of disperse dyes is responsible for their uptake by most adsorbents." Thus peat exhibited good removals for Disperse Red 1 at acidic pH values.

Kinetic studies:

Figure 3 traces the sorption kinetics for the adsorption of each of the four dye types onto peat. For Basic Blue 9, peat exhibited equilibrium times of only 20 minutes with dye removals exceeding 99%. Such a short time for equilibrium, coupled with a high removal indicates a high degree of affinity for this dye group pointing towards chemisorption." For Acid Red 91, peat exhibeted poor removals of just 6% with an equilibrium time of 18 **hours. For Acid** Blue 29 however, peat exhibited a removal of nearly 86% after only 2 hours indicating its effectiveness for basic dyes and certain acidic dyes as well, though the removals for the former type are much better. The values for equilibrium time obtained for peat with Basic Blue 9 and Acid Blue 29 are in agreement with the earlier results obtained by Viraraghavan and Mihial.IO

Peat was highly effective in disperse dye removal with removals exceeding

90%. Peat removed 91% of Disperse Red 1 with an equilibrium time of 6 hours.

The removals exhibited for each of the dyes were compared with the performance of GAC under similar conditions. Amounts of GAC exactly equal to the amounts of peat used, were shaken with similar quantities of dye solutions for times equal to the equilibrium time obtained earlier for each of the dyes. Table III gives a summary of the relative performance in terms of dye removals. As can be seen from Table III, peat exhibited significant removals for Acid Blue 29 though not as good as GAC. But in the case of Basic Blue 9 and Disperse Red 1, the removals by peat were much better than GAC. Disperse dyes are hydrophobic by nature and thereby have a tendency to accumulate at the surface of adsorbents. However, since they are not completely soluble in water, they remain as a dispersion of groups of molecules which prevents them access into the micropores of AC. As a result, the capacity of peat is much better than GAC for disperse dyes, since in the case of peat, it is the external surface area that plays the more significant role compared to the micropores.

Isotherm studies:

The linear form of Langmuir isotherm equation is represented in equation (I).13

$$\frac{1}{X/M} = \frac{1}{Q} + \left(\frac{1}{bQ}\right)\left(\frac{1}{C}\right)$$

Figure 3–Kinetic studies for peat.

Figure 4a–Breakthrough curves for column studies (Peat –Basic Blue 9).

The linearized BET isotherm equation is shown in equation (2).13

$$\frac{C}{(C_x - C)(X/M)} = \left(\frac{1}{BQ}\right) + \left(\frac{B-1}{BQ}\right)\left(\frac{C}{C_s}\right) \tag{2}$$

The linearized Freundlich isotherm equation is shown in equation (3).13

$$\log\left(\frac{X}{M}\right) = \log K + \left(\frac{1}{n}\right)\log C \tag{3}$$

where X/M = amount of solute adsorbed per unit weight of adsorbent(mg/g), C = concentration of solute remaining in solution at equilibrium(mg/L), Cs = saturation concentration of the solute(mg/L), Q = amount of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface(mg/L), b = a constant related to the energy or net enthalpy, K & n = Freundlich constants

and B = constant expressive of the energy of interaction with the surface.

The data obtained from the isotherm studies were tested for applicability to the above three isotherm models. Negative values for the Langmuir and BET isotherm constants indicated the inadequacy of these models to explain the adsorption process, since these constants represent the surface binding energy and monolayer coverage. Table IV gives the best-fit equation co-efficients for all the three models.

From Table IV, it can be observed that Basic Blue 9 conforms to the Freundlich isotherm model for sorption onto peat. For Acid Blue 29 however, sorption onto peat conforms to both the Langmuir and Freundlich models. Disperse Red 1 sorption seems to satisfy all the three adsorption isotherm

models. The removal for Acid Red 91 was very low at 6% and satisfied only the Freundlich model with a R^z value of only 0.3378.

Column studies:

The linearized form of the expression proposed by Thomas for adsorption in a fixed bed column in given in equation (4).14

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_1 q_0 M}{Q} - \frac{k_1 C_0 V}{Q} \tag{4}$$

where C = effluent solute concentration(g/L), Co = influent solute concentration(g/L), k1 = rate constant, q. = maximum solid-phase concentration of the sorbed solute(g/g), M = mass of the adsorbent(g), V = throughput volume(L) and Q = flow rate(L/hr).
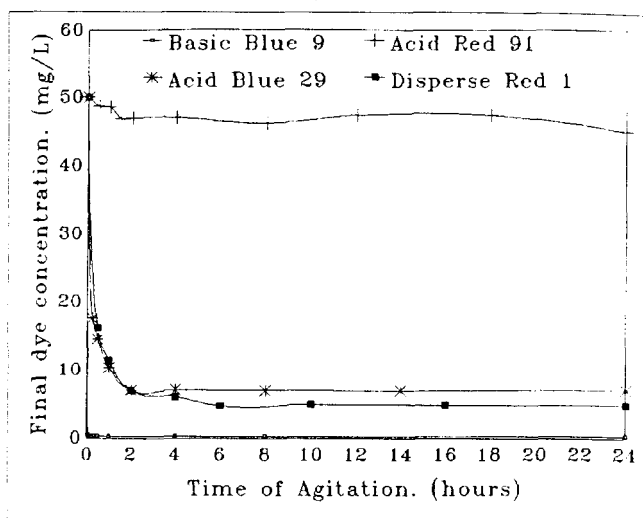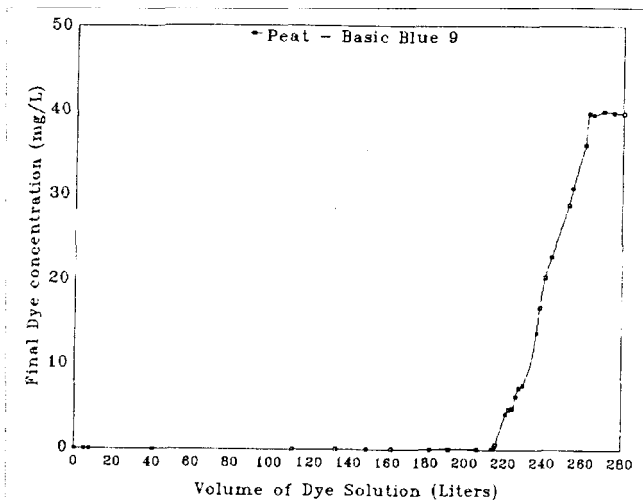
Table III: Comparison of peat's performance with GAC.

Dye	Color removal by peat	Color removal by Granular Activated Carbon
Basic Blue 9	99.3%	64%
Acid Blue 29	**86.0%**	100%
Acid Red 91	**6.0%**	91 .l%
Disperse Red 1	90.5%	**48.6%**

Table IV: Best-fit adsorption isotherm equations.

D y e	Type of Isotherm	Equation	R^2	Applicability
ACID	Langmuir	I(X/M[) = - 918.22 I/C 21.126	0.3375	N . A
RED 91	Freundlich	log (X/M) = -5.468 log C + 8.92	0.3378	A
	B.E.T	C/[(Cs-C)(X/M)]=l2536.38 C/Cs-11296.8	0.2590	N . A
BASIC	Langmuir	I/(X/M) = 0.10005 I/C - 0.2473	0.988	N.A
BLUE 9	Freundlich	log (X/M) = 3.1239 log C + 2.7957	0.9354	A
	B.E.T	C/[(Cs-C)(XJM)]=-0.22821 C/Cs+ 0.0019	0.9592	N.A
ACID	Langmuir	I/(X- = 0.4016 I/C + 0.0717	0.944	A
BLUE 29	Freundlich	log (X/M) = 0.352 log C+ 0.567	0.956	A
	B.E.T	C/[(Cs-C)(X/M)]=O5120 C/Cs-0.05585	0.8397	N.A
DISPERSE	Langmuir	I/(X/M) = 0.2138 I/C + 0.02011	0.9342	A
RED 1	Freundlich	log (X/M) 0.5853logC+0.7147	0.9614	A
	B.E.T	C/[(Cs-C)(X/M)]=O.O614C/C + 0.0023	0.9901	A

A = Applicable. N A = Not Applicable

Table V: Thomas equation coefficients for column run data.

Dye	Adsorbent	Mass of adsorbent	k,	q_o
Acid Blue 29	Peat	**30.70 g**	**33.18**	**0.0088**
Basic Blue 9	Peat	39.46 g	1.0054	**0.326**
Acid Red 91	Peat	31.16g	**52.372**	0.00191

Table V shows the best-fit Thomas equation coefficients obtained for certain adsorbent-dye combinations that showed promise during batch studies.

Figures 4a & 4b show the breakthrough curves for Basic Blue g-Peat and Acid Blue 29-Peat combinations respectively.

The values of q_0 in Table V show that each gram of peat can adsorb as much as 326 mg of Basic **Blue 9 or 8.8 mg of** Acid Blue 29 or 1.91 mg of Acid Red 91. These values indicate good promise for the use of peat as a cheaper alternative for GAC

'Conclusions

The surface charge on the adsorbent and the solution pH play a significant role in influencing the capacity of an adsorbent towards dye ions. As a result, peat was more effective in adsorption of basic dyes than acid dyes.

Disperse dye removal by peat was much better than that by GAC, since the dispersed dye aggregates were too big to enter the micropores of GAC.

The nature of the group which causes acidity or alkalinity to a dye molecule, influences the extent of its adsorption on an adsorbent surface. On a positively charged adsorbent surface, acid dyes with a carbonic group are adsorbed to a greater extent than those with a sulfonic group.
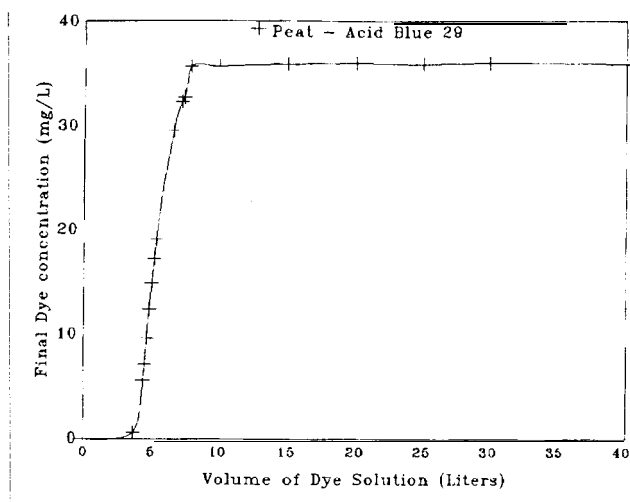
References

(1) Mahloch, J. L., Shlndala, A., McGriff, E. C. and Barnett, W. A., *American Dyestuff Reporter.,* 64(11), 24 (1975).

(2) Gardiner, D. K. and Borne, B. J., *Journal of the Society of Dyers and Colourists.,* 94(8), 339 (1978).

(3) Poots, V. J. P., McKay, G. and Healy, J. J., *Water Research.,* 10. 1061 (1976).

(4) Kouba, J. F. and Zhuang, P., *Fluid/Particle Separation Journal., 7(3), 87* (1994).

(5) Smith, B., Koonce, T. and Hudson, S., *American Dyestuff Reporter., 82(10),* 18 (1993).

(6) Green, F. J.; "The Sigma-Aldrich Handbook of Stains, Dyes and Indicators." Aldrich Chemical Company Inc., Milwaukee (1990).

(7) McKay, G., Allen, S. J., McConvey, I. F. and Otterburn, M. *S., Journal of Colloid and Interface Science., 80(2), 323* (1981).

(8) Valentin, F. H. H., *Filtration and Separation., 23, 224* (1986).

(9) Allen, S. J., *Fuel..* 66, 1171 (1987).

(10) Viraraghavan, T. and Mihial, D. J., *Fresenius Environmental Bulletin., 4, 346* (1995).

(11) Holme, I.; "Developments in the Chemistry and Technology of Organic Dyes." Blackwell Scientific Publications, Oxford, p. 111 (1984).

(12) McKay, G. and Allen, *S. J., Canadian Journal of Chemical Engineering., 62, 340* (1984).

(13) Weber, W. J.; "Physicochemical Processes for Water Quality Control." John Wiley & Sons, New York (1972).

(14) Reynolds, T. D.; "Unit Operations and Processes in Environmental Engineering." Brooks/Cole Engineering Division, Monterey California (1982).

Figure 4b-Breakthrough curves for column studies (Peat -Acid Blue 29).