



DYE REMOVAL USING LOW COST ADSORBENTS

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ABSTRACT

Dyestuff production units and dyeing units have always had a pressing need for techniques that allow economical pretreatment for color in the effluent. The effectiveness of adsorption for dye removal from wastewaters has made it an ideal alternative to other expensive treatment options. The current paper deals with an investigation on four low-cost adsorbents locally available in Saskatchewan, Canada for dye removal. Peat, steel plant slag, bentonite clay and fly ash were utilized for this study and their performance evaluated against that of granular activated carbon. Batch kinetic and isotherm studies, and column studies were undertaken, and the data evaluated for compliance with the Langmuir, Freundlich and BET isotherm models. Synthetic dye wastewaters prepared from commercial grade acid, basic and disperse dyes were used in this study and the results showed high removals of acid dyes by fly ash and slag while peat and bentonite exhibited high basic dye removals. For the acid and basic dyes, the removals were comparable with that of granular activated carbon, while for the disperse dyes, the performance was much better than that of granular activated carbon. The results obtained point towards viable adsorbents which are both effective as well as economically attractive for color removal from wastewaters. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Adsorption; bentonite; dyes; fly ash; peat; slag.

INTRODUCTION

Most of the industries viz. textiles, paper, plastics, leather, food, cosmetics, etc., use dyes or pigments to color their final product. Such extensive use of color often poses problems in the form of colored wastewaters that require pretreatment for color prior to disposal into receiving water bodies or publicly owned treatment works. Even small quantities of dyes can color large water bodies and hence it is much more economical to pretreat a smaller effluent stream for color at the source than after its dilution into a larger water body. While the major generators of colored wastewaters are textile finishing operations, dyestuff production units and pulping mills, this paper is aimed at the former two industries, with an emphasis on removal of excess dyes from the effluent streams.

Most of the commercially used dyes are resistant to biodegradation (Mahloch *et al.*, 1975; Horning, 1977), photodegradation (Gardiner and Borne, 1978) and oxidizing agents (Poots *et al.*, 1976). Unless and otherwise properly treated, these dyes may significantly affect photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life due to the presence of metals, chlorides, etc., in them (Kouba and Zhuang, 1994). The primary concern in any case is the impact of dye color upon

the aesthetics of a receiving water body (McKay, 1980). Although no guidelines for effluent color have been adopted in Canada so far, the possibility for future guidelines for effluent color exists.

While both biological and physical/chemical methods have been employed for dye removal, the former have not been very successful, due to the essential non-biodegradable nature of most of the dyes ((Mahloch *et al.*, 1975; Horning, 1977; Brower and Reed, 1987). The physical/chemical methods that have been proven to be successful are adsorption, coagulation/flocculation, membrane filtration, chemical oxidation and electrochemical treatment.

The present study is aimed at studying the adsorption capacities of locally available low-cost adsorbents from Saskatchewan, Canada for dye removal from wastewaters. The adsorbents employed were horticultural peat, power plant fly ash, steel plant slag and raw bentonite clay, and their performance was evaluated against granular activated carbon (GAC). 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 pH / kinetic / isotherm studies for all dye-adsorbent combinations and subsequent column studies for those dye-adsorbent combinations that showed promise during batch studies. The Langmuir, Freundlich and BET isotherm models were tested for their applicability.

MATERIALS AND METHODS

The dyes utilized for this study were Basic Blue 9 - a cationic thiazine dye, Acid Blue 29 - an anionic disazo dye, Acid Red 91 - an anionic xanthene dye and Disperse Red 1 - a monoazo solvent dye, all supplied by Sigma chemical company, St.Louis, MO, USA. The adsorbents were procured from local sources in Saskatchewan. Horticultural peat was supplied by Saskatchewan Minerals, Carrot River; bentonite clay by Canadian Clay Products Inc., Wilcox; slag by IPSCO Inc., Regina and fly ash samples by Saskatchewan Power Corporation from their Shand power plant. The GAC used in this study was Filtrasorb 400 supplied by Calgon carbon corporation, Pittsburgh, PA, USA.

Synthetic dye wastewaters were prepared by dissolving the different dyes in distilled deionized water at concentrations of 50 mg/l. The peat moss was initially 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 ASTM E:11, #20 sieve prior to their use in experiments. The slag samples and bentonite clay samples were also screened through an ASTM E:11, #20 sieve after grinding in a mortar and pestle prior to their use. Fly ash samples were used as they were received without any pretreatment. All color measurements were made with a Bausch & Lomb-Spectronic 21, spectrophotometer operating in the visible range on absorbance mode. Absorbance values were recorded at the wavelength for maximum absorbance (λ_{\max}) corresponding to each dye and each dye solution was initially calibrated for concentration in terms of absorbance units.

Batch pH studies were conducted by shaking 100 ml of each dye solution with 0.5 g of each of the adsorbents for 24 hours over a range of pH values from 2 to 11. 1N HCl or 1N NaOH was used for pH adjustment. Blanks were run simultaneously, without any adsorbent to determine the impact of pH change on the dye solutions. The dye solutions were shaken in 250 ml glass beakers closed with PARAFILM "M", on a LAB-LINE® orbit shaker operating at 125 rpm. Prior to measurement for color, the dye solutions were filtered through a 1.25 μm glass fiber filter in the case of peat, and centrifuged for 10 minutes at high speed in a Fisher CENTRIFIC™ centrifuge in the case of the other adsorbents. Once the optimum pH was identified, kinetic studies were conducted by shaking 0.5 g of each adsorbent in 100 ml of each dye solution at this optimum pH, for increasing periods of time, until no more dye was removed and equilibrium was achieved. Isotherm studies were conducted by shaking differing quantities of each adsorbent varying from 0.1 g to 1.0 g in 100 ml of each dye solution for a time period equal to the equilibrium time for that particular adsorbent-dye combination. Blank runs, with only the adsorbent in 100 ml of deionized water, were conducted simultaneously at similar conditions to account for any color leached by the adsorbent and adsorbed by the glass container.

RESULTS AND DISCUSSION

pH studies

Figures 1 to 3 show the changes in adsorption capacities of the different adsorbents for each dye with changes in pH. Ionic dyes upon dissolution release colored dye anions/cations in 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.

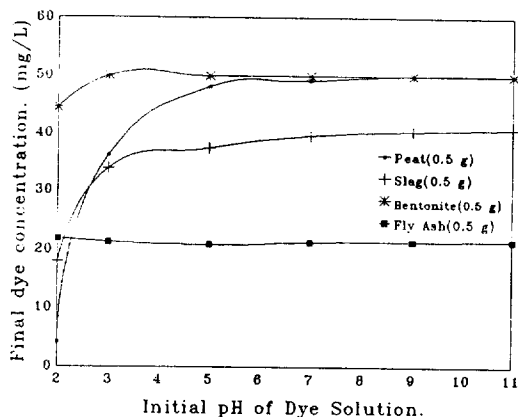


Figure 1. pH studies on Acid Blue 29.

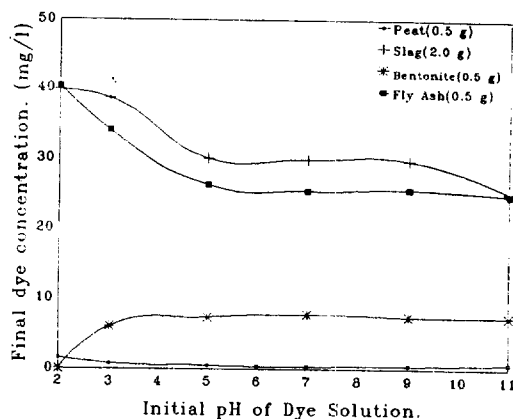


Figure 2. pH studies on Basic Blue 9.

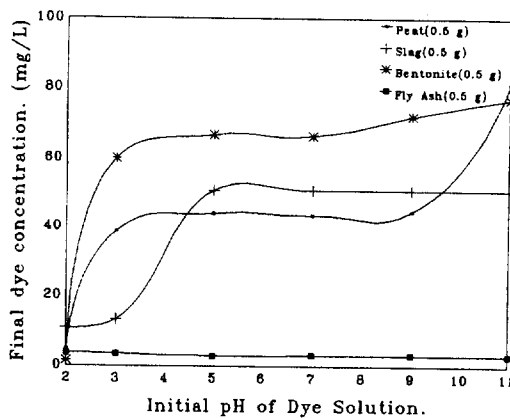


Figure 3. pH studies on Disperse Red 1.

Peat is essentially partially fossilized plant matter composed of lignin and cellulose as its major constituents (Viraraghavan and Ayyaswami, 1987). These constituents, especially lignin, consist of polar functional groups viz. humic and fulvic acids which cause the peat surface to be negatively charged (McKay *et al.*, 1981; Valentin, 1986). Hence, peat surfaces have a 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 also because of an increased competition from protons for these active sites, at lower pH values. Accordingly, the maximum dye adsorption for Basic Blue 9 on peat 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 (Allen, 1987). The observed values also agree well with the results obtained by Viraraghavan and Mihial (1995). 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 hence maximum removal of Acid Blue 29 was observed at pH 2.

Bentonite predominantly consists of montmorillonite which is characterized by a three layer structure of two silicate layers enveloping an aluminate layer. In such a structure, the partial replacement of tetravalent silica with trivalent aluminium and the partial replacement of trivalent aluminium with divalent magnesium leads to unfilled vacant positions which contribute to an excess negative charge on the lattice (Srivastava *et al.*, 1989). Because of this negative charge, bentonite clay exhibited high removals for Basic Blue 9 with removals in excess of 90% at all pH's and exceeding 99.9% at pH 2. This might possibly be due to the precipitation of the basic dye at such a low pH. The acidic dyes studied, namely Acid Blue 29 and Acid Red 91 give rise to colored dye anions in solution. The excess negative charge on the lattice of clay minerals is responsible for the decreased affinity of bentonite clay towards acid dyes. The maximum removal for Acid Blue 29 with bentonite clay was hence observed at pH 2, when the negative charge on the surface is very much reduced due to the excess of protons in solution.

The chief constituents of both fly ash and steel plant slag are metal oxides mainly of Si, Al & Ca. These metal oxides form metal-hydroxide complexes in solution and the subsequent acidic or basic dissociation of these complexes at the solid-solution interface leads to development of a positive or negative charge on the surface (Ahmed, 1966). When the pH of the solution rises, the surface becomes negatively charged and the adsorption capacity for Basic Blue 9 cations increases (Gupta *et al.*, 1990). Hence both steel plant slag and fly ash exhibited maximum removals of the basic dye at pH 11. The adsorption capacities of steel plant slag and fly ash for Basic Blue 9 were however lesser than that of either peat or bentonite clay. At acidic pHs, the dissociation of the metal-hydroxide complexes causes the surface to become positively charged which is very ideal for the removal of anionic dyes. As a result, steel plant slag exhibited maximum removal of Acid Blue 29 at pH 2. In the case of fly ash, the change in initial pH had no noticeable impact on dye removal, since the excess lime in fly ash always increased the final pH to 11.

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, 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. 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 non-removal 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 leads to their uptake by most adsorbents (Holme, 1984). Peat, bentonite clay and steel plant slag exhibited good removals for Disperse Red 1 at acidic pHs. Fly ash again could not be evaluated for the effect of pH, due to its high lime content. In any case, it exhibited removals in excess of 90% for the disperse dye. Since the adsorbents investigated were inexpensive, no recovery and reuse was contemplated. Desorption studies which includes centrifugation may be necessary to examine the separation of the dye from the adsorbent.

Kinetic studies

Figures 4 to 7 show the adsorption kinetics of the different adsorbents for each of the dye types. It can be observed that the concentration of dye remaining in solution decreases with time and at some point in time reaches a constant value beyond which no more of the dye is removed from solution. At this point, the amount of dye being adsorbed onto the adsorbent is in a state of dynamic equilibrium with the amount of dye desorbing from the adsorbent. The time required to attain this state of equilibrium is termed as the equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum dye adsorption capacity of the particular adsorbent under those particular operating conditions.

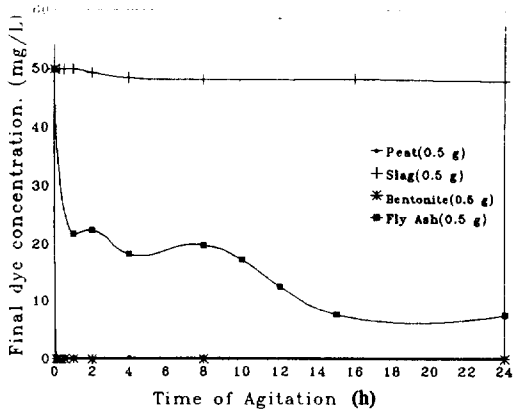


Figure 4. Kinetic studies on Basic Blue 9.

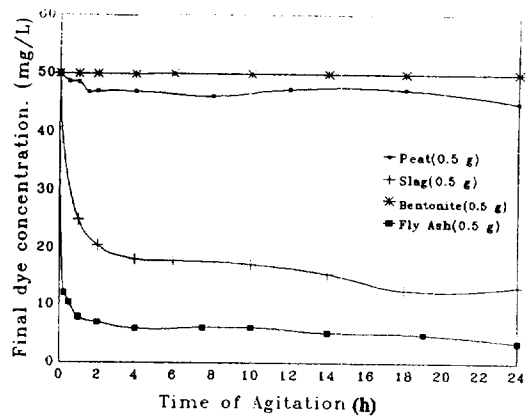


Figure 5. Kinetic studies on Acid Red 91.

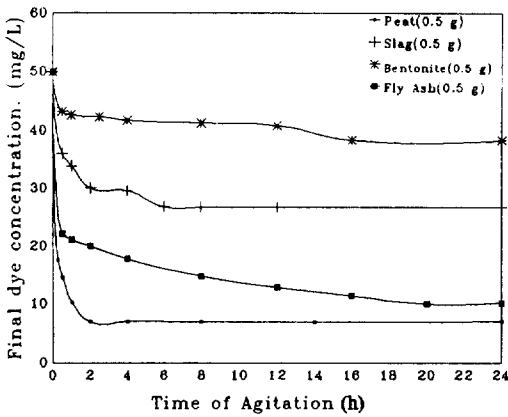


Figure 6. Kinetic studies on Acid Blue 29.

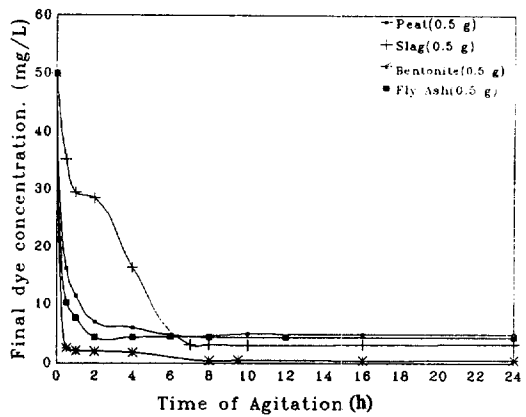


Figure 7. Kinetic studies on Disperse Red 1.

For Basic Blue 9 (Figure 4), peat and bentonite exhibited equilibrium times of 20 minutes and 15 minutes respectively, with dye removals exceeding 99%. Such short times coupled with high removals indicate a high degree of affinity for the dye groups pointing towards chemisorption (McKay and Allen, 1984). However steel plant slag and fly ash took much longer durations of the order of 4 hours and 16 hours respectively, with the corresponding removals being lower at 4% and 61%. Since slag and fly ash surfaces do not inherently have an affinity for cations, the adsorption here is essentially a physical process.

Figure 5 shows the times taken by the adsorbents to attain equilibrium with Acid Red 91. For this acid dye, peat and bentonite clay exhibited poor removals. While bentonite clay did not remove any significant dye at all, peat removed just 6% of dye with an equilibrium time of 2 hours. On the contrary, fly ash and steel plant slag exhibited dye removals as high as 88% and 74%, with equilibrium times of 4 and 18 hours.

Similarly for Acid Blue 29 (Figure 6), bentonite clay exhibited a poor removal of only 23% after 16 hours, while steel plant slag and fly ash showed removals of 46% and 80% after 6 and 20 hours respectively. Peat however exhibited a dye removal of 86% after only 2 hours indicating its effectiveness for both basic and acidic dyes, although the removals for the former type are much better. The equilibrium times obtained for peat with Basic Blue 9 and Acid Blue 29 are in agreement with the earlier results obtained by Viraraghavan

and Mihial (1995). All the four adsorbents were highly effective in Disperse dye removal (Figure 7), with removals exceeding 90%. Peat removed 91% in 6 hours, bentonite clay 99% in 8 hours, steel plant slag 94% in 7 hours and fly ash 91% in 2 hours .

The removals exhibited for each of the dye-adsorbent combinations were compared with the performance of GAC under similar conditions. Amounts of GAC exactly equal to the various adsorbents used, were shaken with similar quantities of dye solutions for times equal to the equilibrium time obtained earlier for each of the dye-adsorbent combination. Table 1 gives a summary of the relative performance in terms of dye removals.

Table 1. Comparison of low-cost adsorbent performance with GAC

Dye	Adsorbent	Color removal by low-cost adsorbent	Color removal by Granular Activated Carbon
Basic Blue 9	Peat	99.3%	64%
	Furnace Slag	4.0%	99.9%
	Bentonite Clay	99.9%	40.26%
	Fly Ash	93.8%	99.9%
Acid Blue 29	Peat	86.0%	100%
	Furnace Slag	46.5%	100%
	Bentonite Clay	23.2%	100%
Acid Red 91	Fly Ash	79.9%	100%
	Peat	6.0%	91.1%
	Furnace Slag	74.0%	99.4%
	Bentonite Clay	0%	99.1%
Disperse Red 1	Fly Ash	88.0%	97.9%
	Peat	90.5%	48.6%
	Furnace Slag	93.8%	48.6%
	Bentonite clay	99.2%	48.6%
	Fly Ash	91.2%	42.15%

Isotherm studies

The Langmuir isotherm is based upon an assumption of monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of the surface (Weber, 1972). The linear form of the Langmuir isotherm equation is represented in equation (1).

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

The B.E.T isotherm assumes multilayer adsorption and that Langmuir equation applies to each layer. Also subsequent layers can be initiated even before a given layer is completely formed (Weber, 1972). The linearized B.E.T isotherm equation is shown in equation (2).

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

The Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage (Weber, 1972). The linearized Freundlich isotherm equation is shown in equation (3).

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

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), C_s = 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.

Tables 2 and 3 give the best-fit equation coefficients for the linearized forms of the three isotherm models for the adsorption of each dye onto each of the adsorbents.

Table 2. Linearized isotherm coefficients for Acid Blue 29 and Basic Blue 9

Adsorbent	ACID BLUE 29						BASIC BLUE 9					
	Langmuir		BET		Freundlich		Langmuir		BET		Freundlich	
	Q	b	Q	B	K	n	Q	b	Q	B	K	n
Peat	13.95	0.178	2.192	-8.17	3.69	2.841	-4.04	-2.47	-4.42	-119.1	624.7	0.32
Bentonite	-1.61	-0.015	0.323	-1.07	43.1x 10 ⁵	0.333	46.30	36.0	2.253	-27.07	43.65	6.30
Slag	-2.36	-0.024	6.254	0.443	37.1x 10 ⁵	0.279	-4.86	-0.005	0.292	-22.09	0.015	0.82
Fly Ash	15.17	0.189	13.76	3.564	1.862	1.361	54.05	0.007	2.486	-6.63	0.431	1.09

Table 3. Linearized isotherm coefficients for Acid Red 91 and Disperse Red 1

Adsorbent	ACID RED 91						DISPERSE RED 1					
	Langmuir		BET		Freundlich		Langmuir		BET		Freundlich	
	Q	b	Q	B	K	n	Q	b	Q	B	K	n
Peat	0.047	-0.023	0.80x 10 ³	-0.11	0.83x 10 ³	-0.18	49.73	0.094	15.70	27.70	5.18	1.71
Bentonite			No removal				22.73	8.445	161.1	16.91	37.72	1.49
Slag	-9.95	-0.026	12.85	1.339	0.044	0.537	33.22	0.094	8.159	89.47	5.13	2.25
Fly Ash	-35.6	-0.049	140.1	0.744	1.485	0.752	30.03	0.106	10.92	21.04	3.71	1.77

Negative values for the Langmuir and BET isotherm constants indicate the inadequacy of the isotherm model to explain the adsorption process, since these constants are indicative of the surface binding energy and monolayer coverage. It was found that in all cases studied, the Freundlich model would be generally applicable. Isotherm data showed that adsorption was the process involved in the removal of dyes from solution.

CONCLUSIONS

This study has provided an insight into the adsorptive capacity of different adsorbents for different types of dyes. The surface charge on the adsorbent and the solution pH play a significant role in influencing the capacity of an adsorbent towards dye ions. Having an excess of negative charge on their surfaces, peat and bentonite clays have a greater capacity to adsorb basic dyes compared to acid dyes. In a similar manner fly ash and steel plant slag have a greater adsorptive capacity for acid dyes than basic dyes.

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.

All the four alternative adsorbents investigated showed much better removal for a disperse dye, compared to GAC. Peat was effective for Basic Blue 9, Disperse Red 1 and Acid Blue 29 in decreasing degrees of removal. Bentonite clay showed good removals for Basic Blue 9 and Disperse Red 1. Steel plant slag had a good adsorptive capacity for Disperse Red 1 and Acid Red 91, while fly ash showed consistently good removals for all four dye types, with maximum removals in case of Disperse Red 1 and Acid Red 91.

ACKNOWLEDGEMENT

This study was supported by a grant from the Natural Sciences and Engineering Research Council of Canada to the second author. The first author thanks the Faculty of Graduate Studies and Research for partial support during the study.

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