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Elimination of Methylene Blue using PVA and Bagasse as Potential Adsorbents

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Abstract

The adsorption capacity of farming (sugarcane) by-product, the bagasse and combination of bagasse and polyvinyl alcohol(PVA) were investigated in batch experiments for the removal of Methylene Blue colorant, with varying parameters like pH and adsorbent dose. The readings were tabulated and the percentage of dye removal was better and more effective with combination of bagasse and PVA in comparison to the bagasse. The optimum percentage of dye removal obtained was 83.42% and 92.81% for 1.0g of bagasse and combination of bagasse and PVA respectively around pH 10. The R^2 values obtained from Freundlich isotherms are 0.9873 and 0.8474 for bagasse and combination of bagasse and PVA adsorbents respectively around pH 10. The R^2 values obtained from Langmuir isotherms are 0.4923 and 0.5826 for bagasse and combination of bagasse and PVA adsorbents respectively around pH 10.

Keywords: adsorbent, adsorption, methylene blue dye, bagasse.

Introduction

Textile industry is one of the foremost contributors to numerous Asian economies including India, as it donates nearly fourteen percent of the total manufacturing production. Textile industry uses a huge amount of water and chemical additives for various manufacturing processes. The leftover chemical additives are discharged into waterbodies in the form of wastewater. Colors are used in every textile industry to color the products. Unused coloring materials are discharged into nearby river bodies with or without treatment. Colored materials such as dyes are low biodegradable and retain for long time in water bodies for a longer period and affect the processes in water bodies. It results in retardation of photosynthesis, growth of aquatic biota by blocking sunlight and thereby decreasing dissolved oxygen content. In dying industry above 30-60 liters of water is consumed per kg of cloth dyed and large quantities of effluents are released during process. Its amount is to be about 16 % of the total water consumed in the mill. Several methods have been developed for the elimination of dye from wastewater, among that adsorption plays an important role.

Adsorption

Adsorption is a process of accretion of large number of molecules on the exterior surface of the liquid or solid part of an adsorbent. Adsorption takes place due to the unbalanced forces at the surface of the adsorbent. Adsorption process involves two mechanism adsorbent and adsorbate. Adsorbent is the material which adsorption takes place. Adsorbate is the matter which is being adsorbed on the adsorbent. Adsorbate gets adsorbed on the adsorbent. Adsorption can be differentiated based on forces existing between adsorbate and adsorbent are as follows:

a. Physical adsorption
b. Chemical adsorption

In physical adsorption there are weak vanderwaal forces acting on molecules of adsorbate and adsorbent, whereas in chemical adsorption there are chemical forces acting on adsorbate and adsorbent.

Adsorption Isotherms

Isotherm is a line of connecting points of equivalent temperature at a given period of time.

Adsorption isotherms are the graphs plotted for the study, it is plotted against amount of adsorbate adsorbed on the surface of adsorbent and pressure at constant temperature. The different adsorption isotherms are Freundlich, Langmuir and BET theory.

$$\text{Adsorbate} + \text{Adsorbent} \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} \text{Adsorption}$$

$$A + B \rightleftharpoons AB$$

Le-chatelier's principle says that direction of equilibrium shifts in the direction of stress.
Figure shows the basic adsorption isotherm.

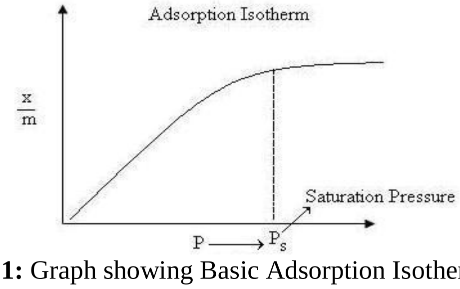

Figure 1: Graph showing Basic Adsorption Isotherm

Freundlich gave an empirical formula for gases adsorbed by unit mass of solid as adsorbent. The equation is known as Freundlich Adsorption Isotherm.

$$q_e = K_f \cdot C_e^{1/n}$$

Where,

q_e = quantity of metal adsorbed at equilibrium.
K_f=Freundlich capacity factor.
1/n = Freundlich concentration parameter.
C_e = Equilibrium concentration in mg/L.

Equation can be written in linear form as:

$$ln q_e = \frac{1}{n} \ln C_e + \ln K_f$$

K_f and n are determined by plotting Ce against qe.

Langmuir gave an empirical formula based on studies conducted for monolayer adsorption, whenever a gas is in contact with a solid there will be an equilibrium established between the molecules in the gas phase and the corresponding adsorbed species (molecules or atoms) which are bound to the surface of the solid. This model is expressed using equation:

$$q_e = \frac{q_{max} b C_e}{(1 + bC_e)}$$

Where,

q_e= is the quantity of metal adsorbed at equilibrium.
q_{max} = the maximum adsorption capacity.
C_e = Equilibrium concentration in mg/L.
b = constant that characterizes the attraction between the adsorbent and the metal ion.

Equation can be written in linear form as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max} b}$$

C_e against C_e/(x/m) are plotted to determine the values of $q_{max}$and b.

Brunaur-emmett-teller (BET) theory aims to explain the multilayer adsorption. At high pressure and low temperature, thermal energy of gaseous molecules reduces thereby more gaseous molecules accumulating on the adsorbent.

The BET equation is given as;

$$V_{total} = \frac{V_{mono} C \left(\frac{P}{P_0}\right)}{\left(1 - \frac{P}{P_0}\right)\left(1 + C\left(\frac{P}{P_0}\right) - \frac{P}{P_0}\right)}$$

Another form of BET equation is

$$\frac{P}{V_{total}(P - P_0)} = \frac{1}{V_{mono} C} + \frac{c-1}{V_{mono} C}\left(\frac{P}{P_0}\right)$$

Where P and P_0 are the equilibrium and saturation pressure. V_{mono} be the adsorbed volume of gas at high pressure conditions.

Biosorbtion

Biosorption is a physico-chemical procedure that happens logically in certain biomass which allows it to inertly focus and bind impurities onto its cellular assembly. Bagasse is the dry pulpy filtrate left after the withdrawal of juice from sugarcane.

Polymers

A polymer is a macromolecule, contains many repeated subunits, bounded by covalent bonds. Polyvinyl alcohol is a water-soluble synthetic polymer. It is used in papermaking, textiles, and a variety of coatings. It is white and odourless. Polyvinyl alcohol is used as an emulsion polymerization aid, as protective colloid to make polyvinyl acetate dispersions. Polyvinyl alcohol is used as paper adhesive with boric acid in spiral tube winding and solid board production.

Methods

Materials and Methods

Preparation of Biosorbent

Bagasse was brought from “Karnataka Municipal Office, Chikmagalur” and was washed with water continuously for 2 hours. It is then sun dried for 7 hours and oven dried for 7 hours at 110°C. Bagasse was saturated in distilled water for 48 hours with frequent change of distilled water for every 12 hours. To make bagasse free of lignin it was soaked in alkali for 12 hours, continued by washing with distilled water, in order to prevent the color interference, it is treated with formaldehyde. Then the material was oven dried at 50-60°C for 24 hours and sundried for 6 hours and this dried material was grounded into fine powder (250-500µm) and used as raw bagasse adsorbent.

Combination of PVA and Bagasse

Poly vinyl alcohol of molecular weight 72000-100000g/mol is used as an adsorbent. 10gm of PVA was mixed with 90ml of water and boiled at 80°C in hot water bath for 30-45mins and stirred at frequent intervals. Prepared swollen gel was mixed with measured quantity of raw bagasse.

Figure 2: Combination of PVA and bagasse

Preparation of Stock Solution

1ml of alkaline Methylene Blue dye was mixed with 1000ml of water. The pH of the prepared stock solution was adjusted to different values by adding 0.1N Hydro-Chloric acid or 0.1N Sodium Hydroxide. The pH values are taken around 2, 4, 6, 8, 10, and 12.

Figure 3: Preparation of stock solution

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Methodology

- The initial concentration of the stock solution was measured by Spectro-photometer under 455nm of program number 120.
- 250ml of stock solution was taken in 6 beakers. The raw bagasse and combination of PVA and bagasse was weighed as 0.2, 0.4, 0.6, 0.8, 1.0, 1.2gm.
- The jar test apparatus was calibrated to 200rpm. The mixing was carried out for 6 hours.
- The solution in the beakers was kept for 10 min under calm condition. The percentage removal efficiency was calculated.

Figure 4: Jar test apparatus

Results

Batch Mode Adsorption Experiments

The percentage removal of Methylene blue by using bagasse and combination of PVA & bagasse is determined and are tabulated below.

Table 1: decrease in concentration of Methylene Blue at pH 2

Adsorbent dosage(g)	Concentration of MB in Pt-Co ph6			% Removal of MB by adsorbent	
	Initial	Final (Bagasse)	Final (PVA+ Bagasse	Bagasse	Combination of PVA & Bagasse
0.2	181	136	105	24.86	41.98
0.4	181	124	87	31.49	51.93
0.6	181	92	50	49.17	72.37
0.8	181	72	30	60.22	83.42
1	181	38	21	79.0	88.39
1.2	181	37	20	79.55	88.95

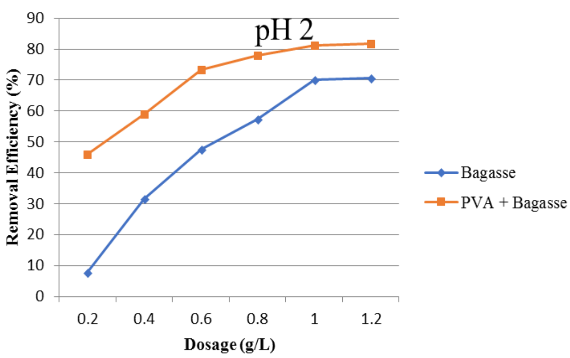

Figure 5: decrease in concentration of Methylene Blue at pH 2

Table 2: decrease in concentration of Methylene Blue at pH 4

Adsorbent dosage(g)	Concentration of MB in Pt-Co (ph4			% Removal of MB by adsorbent	
	Initial	Final (Bagasse)	Final (PVA +Bagasse	Bagasse	Combination of PVA & Bagasse
0.2	181	150	97	17.12	46.40
0.4	181	136	74	24.86	59.11
0.6	181	98	42	45.85	76.79
0.8	181	86	38	52.48	79.00
1	181	50	30	72.37	83.42
1.2	181	49	29	72.92	83.9

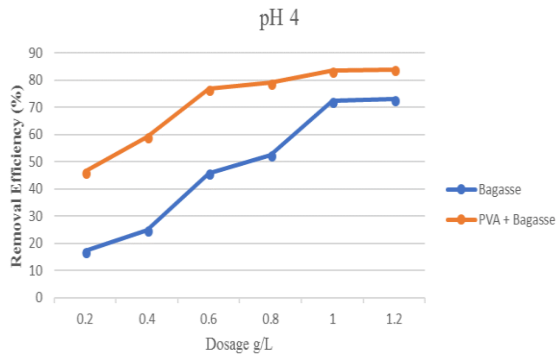

Figure 6: decrease in concentration of Methylene Blue at pH 4

Table 3: decrease in concentration of Methylene Blue at pH 6

Adsorbent dosage(g)	Concentration of MB in Pt-Co ph2			% Removal of MB by adsorbent	
	Initial	Final (Bagasse)	Final (PVA+ Bagasse	Bagasse	Combination of PVA & Bagasse
0.2	181	167	198	7.73	45.85
0.4	181	124	74	31.49	59.11
0.6	181	95	48	47.51	73.48
0.8	181	77	40	57.45	77.90
1	181	54	34	70.16	81.21
1.2	181	53	33	70.71	81.76

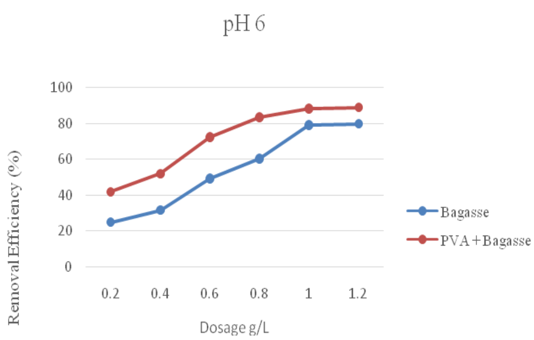

Figure 7: decrease in concentration of Methylene Blue at pH 6

Table 4: decrease in concentration of Methylene Blue at pH 8

Adsorbent dosage(g)	Concentration of MB in Pt-Co ph 8			% Removal of MB by adsorbent	
	Initial	Final (Bagasse)	Final (PVA +Bagasse	Bagasse	Combination of PVA & Bagasse
0.2	181	106	74	41.43	59.11
0.4	181	85	52	53.03	71.27
0.6	181	73	43	59.66	76.24
0.8	181	52	25	71.27	86.18
1	181	37	20	79.55	88.95
1.2	181	38	19	79.00	89.50

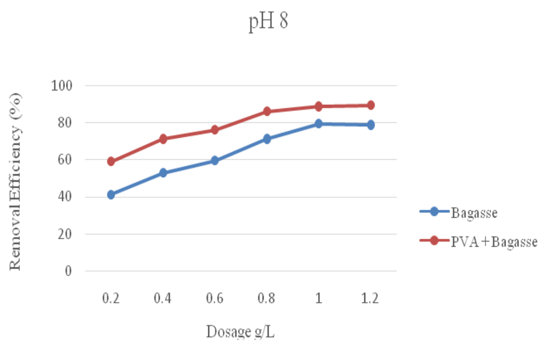

Figure 8: decrease in concentration of Methylene Blue at pH 8

Table 5: Effect of Contact Time on Percentage removal of Methylene blue at pH 10.

TimeMin	Concentration of MB in Pt-Co			% Removal of MB	
	Initial	Final Bagasse (1.2g)	Final PVA+Bagasse (1.2g)	Bagasse	PVA+ Bagasse
10	181	134	126	25.9	30.38
20	181	128	113	29.2	37.56
30	181	114	98	37.01	45.85
40	181	103	79	44.3	56.35
50	181	94	70	48.06	61.66
60	181	87	63	51.93	65.19
70	181	68	52	62.4	71.27
80	181	67	51	62.9	71.81

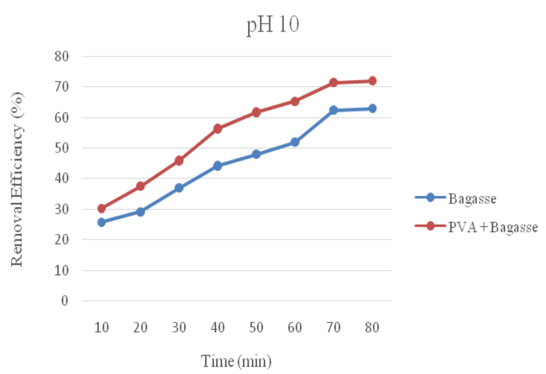

Figure 9: Percentage removal of Methylene Blue at pH 10 with respect to contact time

The removal efficiency and specific uptake of methylene blue dye depend upon type and quantity of the adsorbent. The quantity of adsorbent dosage was varied from 0.1 to 1.2 g/250 ml. The percentage removal of methylene blue due increased with increase in adsorbent dosage and pH, further increase in the amount of adsorbent dosage beyond 1.0 g/250 ml there was a negligible increase in dye removal. Considering these results, a dose of 1g/250ml was considered sufficient, for the optimal removal of methylene blue and pH beyond 10±0.5 precipitate formation occurred, due to this reason adsorption was not studied beyond pH 10±0.5.

Adsorption Isotherms

Experimental equilibrium adsorption data were tested for Langmuir and Freundlich equations/isotherms.

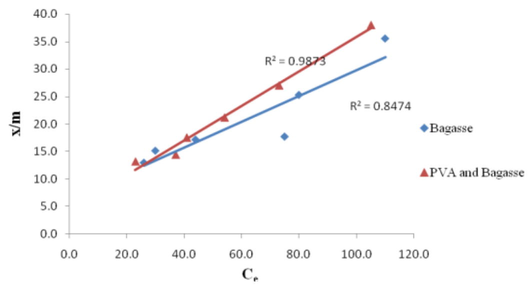

Figure 10: Freundlich isotherm plotted for q_e vs. C_e

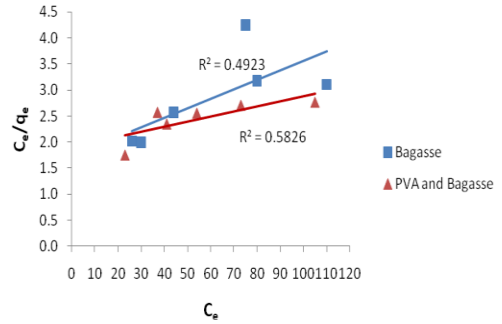

Figure 11: Langmuir isotherm plotted for C_e/q_e vs. C_e

Table 6: The Freundlich model parameters

	b	q_{max}	R^2	R_L
Bagasse	0.018	12.92	0.582	0.190
PVA + Bagasse	0.009	13.17	0.492	0.275

Table.7: The Langmuir model parameters

	n	k_f	R^2
Bagasse	4.273	6.026	0.847
PVA + Bagasse	3.184	8.593	0.987

Relationship between R_L and the type of isotherm can be given by the conditions like $R_L>1$ unfavorable condition exists, if $R_L=1$ then linear isotherms are identified, if condition is $0<R_L<1$ then isotherm condition is favorable, if $R_L=0$ then isotherm condition is irreversible.

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