Carbon Science
Vol. 8, No. 1 March 2007 pp. 1-5

Removal of Dyes by Biosorption on Biomass Ash

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(Received January 17, 2007; Accepted March 5, 2007)

Abstract

The use of low cost and ecofriendly adsorbent has been investigated as an alternative to the current expensive method of removing dyes from wastewater. Cow dung cakes were collected from the nearby village which was burnt in a muffle furnace at 500°C to obtain the required ash. This paper deals with the removal of Reactive Blue 221, Acidoll Yellow 2GNL and Olive BGL which are mainly used in textile industry, from aqueous solution by cow dung ash without any pretreatment. The adsorption was achieved under different pH, adsorbate concentration and the applicability of Langmuir and Freundlich isotherms were examined.

Keywords : *Adsorption, Cow dung ash, Textile dyes, Isotherms*

1. Introduction

The coloration and brightening of natural and man made fibers by dyeing leads to a lot of wastewater in the dyeing mill. Color is a major pollutant in this water as it has high BOD and COD levels, solids, oil and possibly toxic organics including phenols from dyeing and finishing. Color/dye persists for long distances in flowing water, effects photosynthetic activity and aquatic plant and animal life.

The process of adsorption has received considerable attention and of late has become one of the most popular methods of removing color from wastewater. Many studies have been carried out by different workers on adsorption of color compounds from their aqueous solutions using low cost adsorbents. As compared to the activated carbon, the carbon obtained from bio-waste such as cow dung ash, banana pith, rice husk, sugarcane dust etc. is cheaper, readily and abundantly available around and more environment friendly. It is also a method of bringing into use the potentially discarded material.

Vadivelon and Kumar [1] carried out batch experiments for the sorption of methylene blue onto rice husk particles. The sorption process was found to be controlled by both surface and pore diffusion. Ho, Chiu and Wong [2] studied the adsorption of three basic dyes Basic Violet 10, Basic Violet 1 and Basic Green 4 from aqueous solution onto sugarcane dust. The tests revealed the potential of sugarcane dust, a waste material, to be a low cost adsorbent. Namasivayam and Kavitha [3] carried out the adsorption of congo red on coir pith carbon by varying the parameters such as dye concentration, pH, agitation time, temperature and adsorbent dose. Acidic pH was favorable for the adsorption of congo red and the study suggested that chemisorption might be the major mode of adsorption. Sivaraj, Sivakumar, Senthilkumar and Subbuam [4] found that H_3PO_4 impregnated activated carbon from cassava peel (an agricultural waste from the food processing industry) showed higher efficiency than heat treated in the adsorption of dyes and metals. Sivaraj, Namasivayam and Kadirvelu [5] studied the effectiveness of orange peel in adsorbing Acid Violet 17 from aqueous solutions and found that adsorption increased with the increase in the pH. Wong [6] studied the effects of different methods for fly ash treatment using conventional chemical, sonochemical and microwave method on three basic dyes (methylene blue, crystal violet and rhodamine blue) and shown that fly ash exhibited different adsorption capacity depending on types of dyes. Nassar [7] studied the rate of intraparticle diffusion for adsorption of two basic dyes, Basic Red and Basic Yellow, on particles of palm fruit bunch and the adsorption process was found to be diffusion controlled process.

The present work forms a part of a continuing study of removal of dyes by adsorption.

2. Experimental

Adsorption studies were performed by the batch technique using cow dung ash (a low cost bio-waste) as an adsorbent without giving any pretreatment. A stock solution of the dyes with a concentration of 1000 mg/L was prepared and dilutions were made with distilled water to make different concentrations (10-100 mg/L) for the adsorption studies. A known weight of the adsorbent (1 g) was added to 50 mL of each of the above concentration in 100 mL measuring flasks. These were placed in an air thermostat for 24 hrs. with occasional shaking. The samples were then filtered and analyzed using UV-spectrophotometer (Elico CL54D). Wavelengths of different dyes were determined by λ_{max} method. The pH values of solutions were adjusted by addition of H_2SO_4 and NaOH.

3. Results and Discussion

3.1. Effect of initial dye concentration

Effect of initial dye concentration was studied and is given in Table 1, from which it is obvious that as concentration of the dye increases the amount of each dye adsorbed per gram of the adsorbent also increases for all pH values. But the percentage of adsorbed dye per gram of adsorbent decreases as concentration increases for all the three dyes studied.

For each dye, amount adsorbed per gram of adsorbent is increasing with increasing concentration of dye but this amount is different for different dyes. For Acidoll Yellow 2GNL amount adsorbed per gram is maximum while for Olive BGL, it is minimum at all three pH values.

3.2. Effect of pH

Table 1 also indicates that the pH change has a marked effect on the adsorption of dyes. At different pH values the amount adsorbed per gram of the adsorbent is different. For Reactive Blue 221 the amount of dye adsorbed is maximum at pH 10.05 (38.8 mg/g) while it is minimum at pH 5.61 (22.0 mg/g). For Acidoll Yellow 2GNL strong acidic condition i.e. pH 2.35 shows maximum adsorption (54.2 mg/g) whereas at mild acidic condition i.e. pH 4.15 adsorption is least (35.3 mg/g). Interestingly for Olive BGL both acidic and basic condition exhibits favorable adsorption than the neutral condition of the dye solution.

3.3. Data fit for Simple Isotherms

The experimental data for the dyes studied were fitted to the Polynomial of the type:

$$Q_e=A+B_1C_e+B_2C_e^2+\cdots+B_4C_e^4 \quad (1)$$

The values of the constants A, B_1, B_2,….. B_4 along with the coefficient of correlation, R^2 and standard deviation, SD

Table 1. Concentration of dyes (C_e) and amount of dye adsorbed per gram of the adsorbent (Q_e) at different pH

Dye Name	REACTIVE BLUE 221			ACIDOLL YELLOW 2GNL			OLIVE BGL		
	Q_e (mg/g)								
	pH			pH			pH		
C_e (mg/L)	**4.32**	**10.05**	**5.61**	**2.35**	**8.62**	**4.15**	**3.32**	**6.60**	**9.97**
10	5.2	6	3	6.4	6	6.6	3.2	1	2.6
20	12.2	8.6	5.84	12.3	11.8	12.4	5.4	3	5
30	14.6	12.87	7.42	16.8	20.0	17.6	7.2	4.2	6.4
40	17	16.21	8.9	20.3	22.4	22.4	8.08	5.62	8.2
50	19.95	19.4	10.59	24.4	28.2	26.4	10.48	7.1	9.8
60	22.7	24.27	12	30.3	31.8	29.4	11.22	8.4	11.66
70	24.38	25.64	14.25	35.4	35.6	31.1	13.97	9.06	14
80	27.05	30.56	15.6	41.3	38.4	32.2	15.6	10	15.11
90	28	33.9	17.4	45.8	42.6	34.2	17.73	12.06	16.38
100	28.6	38.8	22	54.2	45.0	35.3	18.3	14.14	18

Table 2. Values of different constants for polynomial fit data

Constant	REACTIVE BLUE 221			ACIDOLL YELLOW 2GNL			OLIVE BGL		
	pH			pH			pH		
	4.32	**5.61**	**10.05**	**2.35**	**4.15**	**8.62**	**3.32**	**6.60**	**9.97**
A	−3.75417	0.88251	4.01667	0.21667	1.2425	−2.73333	−0.58083	−0.41333	0.42083
B_1	1.1549	0.22785	0.11021	0.71916	0.50018	0.94135	0.4759	0.13285	0.25233
B_2	0.0257	6.619E-04	0.00915	−0.00869	0.00505	−0.00985	−0.01162	0.00219	−0.00256
B_3	3.07E-04	−4.27E-05	−1.32E-04	1.026E-04	−1.34E-04	7.78E-05	1.643E-04	−5.38E-05	3.579E-05
B_4	−1.34E-06	3.41E-07	6.51E-07	−3.40E-07	6.84E-07	−2.5E-07	−7.67E-07	3.32E-07	−1.79E-07
R^2	0.99623	0.99595	0.99755	0.99838	0.99949	0.9968	0.99661	0.99771	0.99779
SD	0.63559	0.4912	0.7258	0.83358	0.29596	0.98772	0.40678	0.26345	0.32583

are given in Table 2 for the three dyes respectively.

Fig. 1 shows that for Reactive Blue 221, pH 4.32 and 5.61 tend to get stable at a higher concentration and are better suited whereas pH 10.05 shows a linear behavior in the adsorption. It is obvious from the same that acidic pH is better at lower dye concentration and basic pH is better for higher concentration.

The results from fitting to polynomial for simple isotherms are given in Table 2.

Fig. 2 shows that for Acidoll Yellow 2GNL highly acidic pH (2.35) is best suited for the adsorption of dye while mild acidic pH (4.15) and basic pH (8.62) are least suited as the adsorption tends to get leveled.

For Olive BGL (Fig. 3) it can be easily drawn that the simple isotherm shows the same behavior for all the three pH values that is with increase in concentration the adsorption of dye also increases. Both acidic (3.32) and basic (9.97) pH values are better suited than the neutral condition (6.60). But acidic solutions favour better adsorption from other pH values.

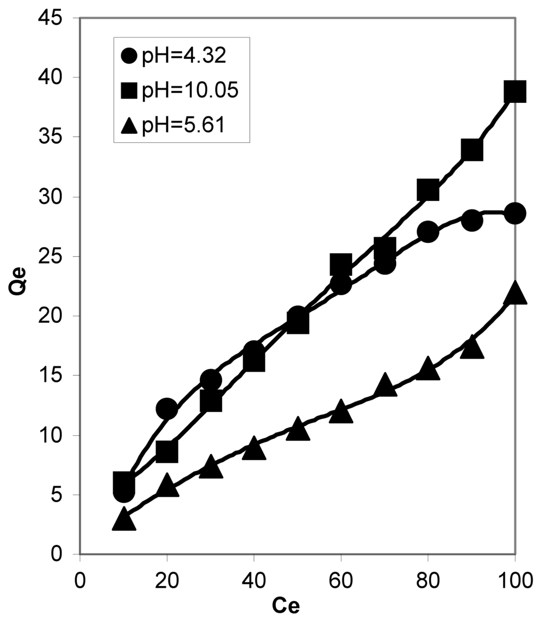

Fig. 1. Adsorption isotherm of Reactive Blue 221 at different pH values.

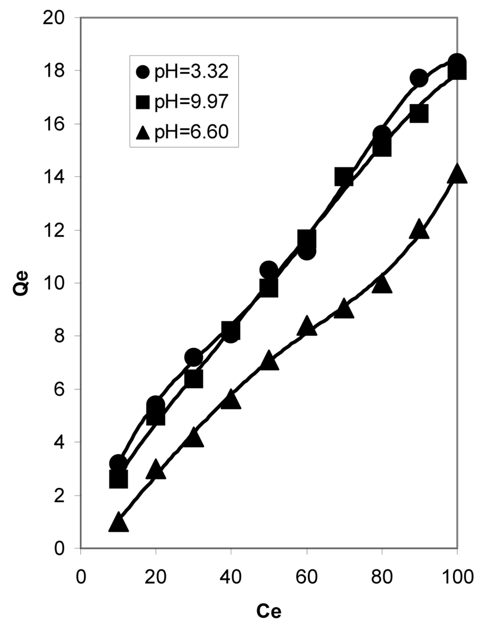

Fig. 3. Adsorption isotherm of Olive BGL at different pH values.

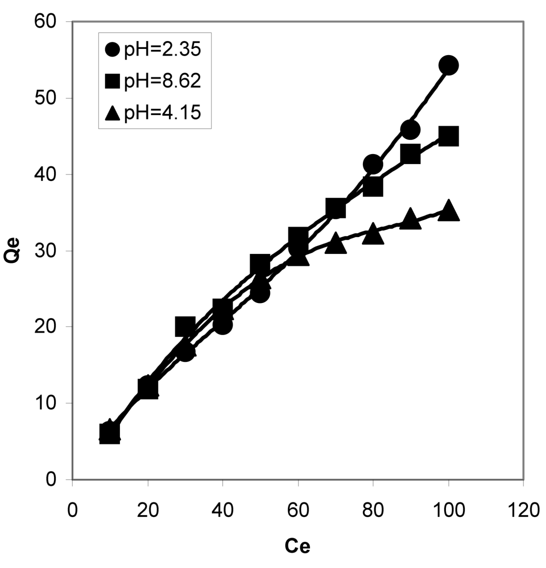

Fig. 2. Adsorption isotherm of Acidoll Yellow 2GNL at different pH values.

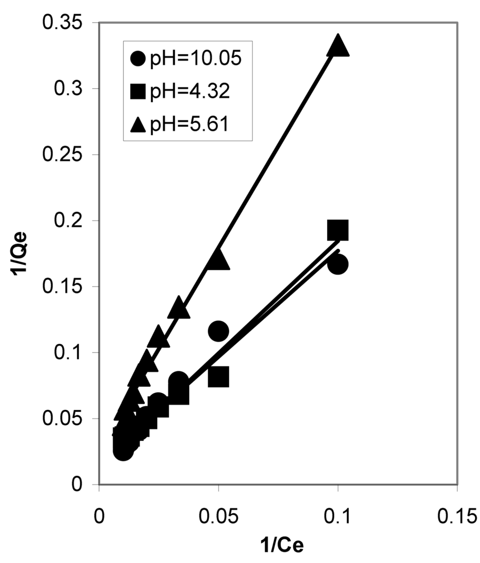

Fig. 4. Langmuir isotherm of Reactive Blue 221 at different pH values.

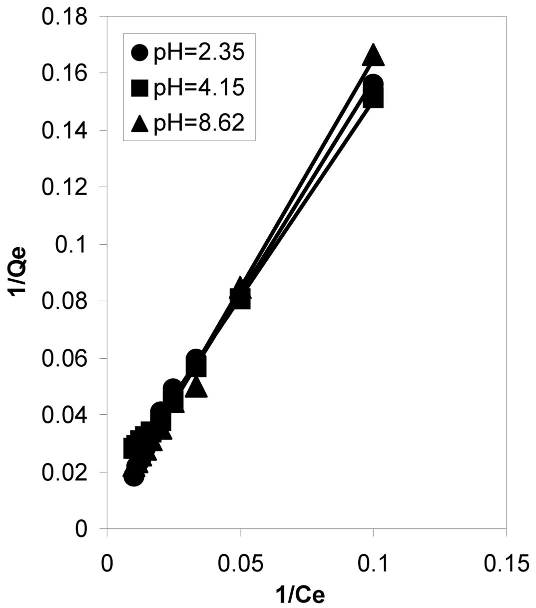

Fig. 5. Langmuir isotherm of Acidoll Yellow 2GNL at different pH values.

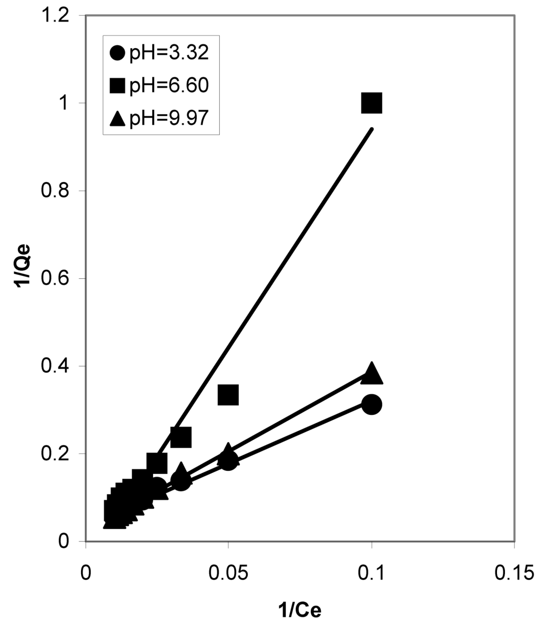

Fig. 6. Langmuir isotherm of Olive BGL at different pH values.

3.4. Langmuir isotherms at various pH

The data obtained was fitted to the Langmuir isotherm as shown in Fig. 4, 5 and 6 for Reactive Blue 221, Acidoll Yellow 2GNL and Olive BGL respectively at three different pH values. From these plots adsorption capacity and energy of adsorption were calculated.

Table 3 gives the values of the Langmuir constants "Q" (adsorption capacity in mg/g) and "b" (energy of adsorption in mg/L) along with the dimensionless separation factor R and SD for the three dyes studied.

3.5. Freundlich isotherm at various pH

The data was also fitted to the Freundlich isotherm as shown in Fig. 7, 8 and 9 for the three dyes respectively at various pH values. Freundlich constants "K_F" (adsorption capacity) and "n" (process intensity) have also been calculated from the slope and intercept of log these plots and their values along with R and SD are given in the Table 4.

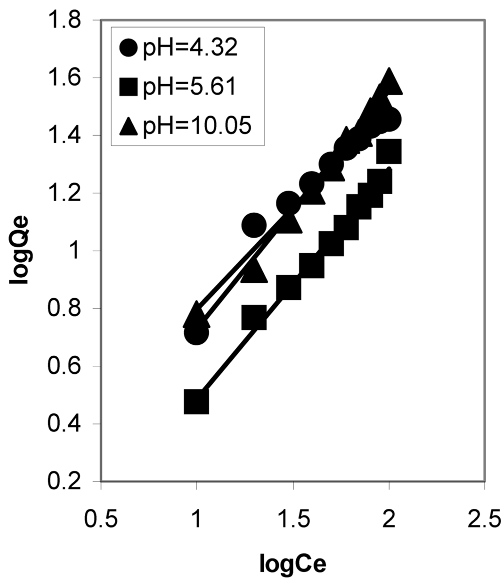

Fig. 7. Freundlich isotherm of Reactive Blue 221 at different pH values.

Table 3. Values of different constants for Langmuir isotherms at various pH

Dye Name	Reactive blue 221			Acidoll yellow 2GNL			Olive BGL		
parameter	pH			pH			pH		
	4.32	**10.05**	**5.61**	**2.35**	**8.62**	**4.15**	**3.32**	**9.97**	**6.60**
R	0.98995	0.98175	0.9968	0.99795	0.99792	0.99909	0.993	0.99831	0.98553
SD	0.00713	0.00912	0.00722	0.00283	0.00305	0.00173	0.00997	0.0062	0.0503
Q	67.7966	57.7367	37.1471	135.8696	235.2941	82.1018	28.0347	40.9332	−18.5494
b	0.008694	0.010819	0.008786	0.004905	0.002647	0.00816	0.012514	0.006747	−0.00542

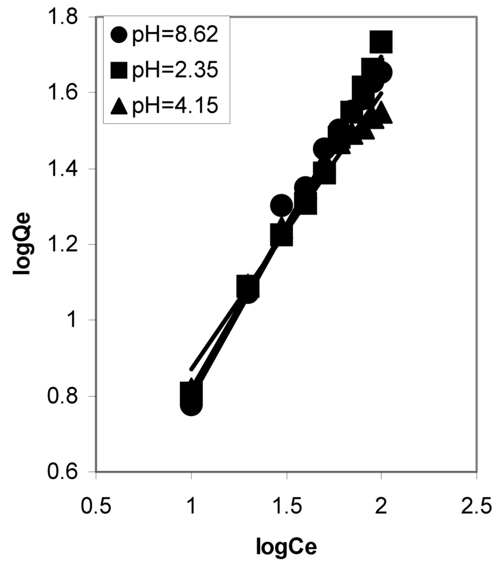

Fig. 8. Freundlich isotherm of Acidoll Yellow 2GNL at different pH values.

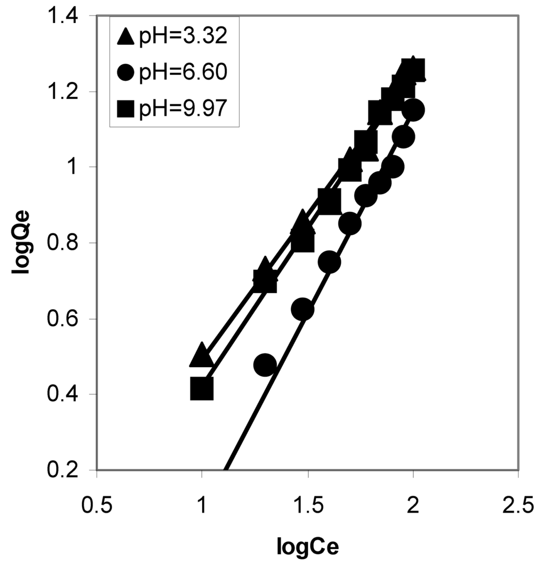

Fig. 9. Freundlich isotherm of Olive BGL at different pH values.

Table 4. Values of different constants for Freundlich isotherms at various pH

Dye Name	Reactive blue 221			Acidoll yellow 2GNL			Olive BGL		
parameter	pH			pH			pH		
	4.32	**10.05**	**5.61**	**2.35**	**8.62**	**4.15**	**3.32**	**9.97**	**6.60**
R	0.98231	0.99446	0.9942	0.99677	0.99356	0.988	0.99569	0.99873	0.99161
SD	0.04521	0.02956	0.02918	0.02444	0.03331	0.03844	0.02401	0.01424	0.04703
K_F	1.099208	0.905435	0.730767	0.902966	0.955491	1.152807	0.761283	0.661252	0.372254
n	1.423893	1.207729	1.251314	1.113016	1.155789	1.373343	1.309106	0.76388	1.309106

4. Conclusions

Adsorption of the dyes studied on Cow Dung ash shows that with increase in the concentration of dye there is decrease in the percentage removal of the dye per gram. Adsorption of dye showed marked effect with pH change as Reactive Blue 221 was adsorbed maximum at pH 10.05, Acidoll Yellow 2GNL showed maximum adsorption at pH 2.35 whereas for Olive BGL both acidic (3.32) and basic (9.97) pH showed similar adsorption which was better than the neutral (6.60) pH. The three dyes obey the Langmuir and Freundlich isotherms and the pH value of the dye solution has a marked effect on the applicability of these isotherms. Reactive Blue 221 at pH 5.61, Acidoll Yellow 2GNL at pH 4.15 and Olive BGL at pH 9.97 are best fitted to the Langmuir equation whereas these are best fitted to the Freundlich equation at pH 10.05, 2.35 and 9.97 respectively.

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