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Full Length Research Paper

Removal of Erichrome Black T from aqueous solution using low cost waste biomass (cow dung ash) at 303 and 308K

Rashid Mahmood* and Afia Naseer

Division of Science and Technology, University of Education, Township Lahore-54000, Pakistan.

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Waste biomass cow dung ash was used as an adsorbent for the removal of Erichrome Black T (EBT) from aqueous solution using simple batch technique. The contact time in terms of adsorption capacity was optimized at 303 and 308K, respectively and it was found to be 60 min for both temperatures. All the experiments were carried out at pH = 7. The adsorption capacity of EBT increased from 0.20 to 0.75 and 0.2 to 0.8 mg/g with 1 g of adsorbent at 303 and 308K, respectively by increasing concentration from 2 to 10 mg/L. The data were employed to Langmuir and Freundlich adsorption isotherm models and because of higher regression co-efficient R^2 values at both temperatures the Langmuir adsorption isotherm was found to be well fitted to the data. The adsorption was found to be spontaneous and endothermic at 308K due to negative free energy and positive enthalpy.

Key words: Erichrome Black T, cow dung, adsorption, thermodynamic parameters.

INTRODUCTION

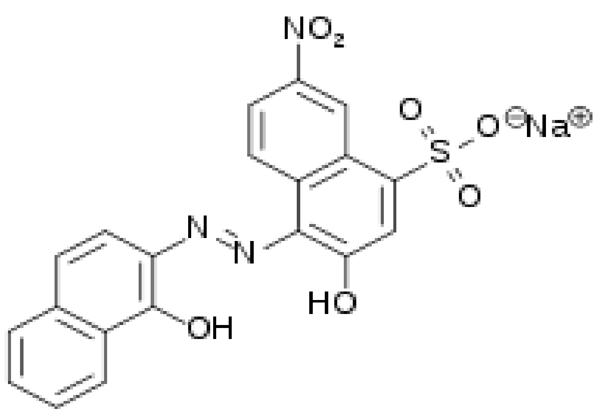
The industries like, textile, paper, printing, leather, food, cosmetics etc, use dyes to color their final products. Discharge of such colored effluents imparts color to the receiving water bodies (River and Lakes) and interferes with its intended beneficial use. Waste water containing even a small amount of dyes can severely affect the aquatic life due to the reduction of light penetration and their toxicity (Mamdouh and Geundi, 1991). Amongst the various techniques such as, coagulation (Weber, 1978), ultra-filtration (Malakootian and Fatehizadeh, 2010), and photo-oxidation (Rajeev and Varshney, 2006), the adsorption is recognized as an efficient, promising and most widely used technique for the treatment of industrial waste water containing color and other organic impurities. The chemical composition of the waste biomass (Stanisiav et al., 2010) is significant for its use as an adsorbent for the purification purpose and the use of waste biomass is highly cost effective as compared to the commonly used adsorbent that is, activated charcoal. Sorbents such as Rosewood Sawdust, Saw dust, Trichoderma Harzianum, Pithophora sp. (fresh water algae), Hydrialla Verticillata and Luffa Cylindrica (Garg et al., 2004; Chakraborty et al., 2005; Sadhasivam et al., 2007; Kumar et al., 2005; Rajeshkhannan et al., 2009, Marchetti et al., 2000) sugar cane dust; algae, red algae (Sari and Tuzen, 2008a), macro fungus (Anayurt et al., 2009), green alga (Sari and Tuzen, 2008b), banana and orange peels (Annadurai et al., 2002) and lichen (Sari et al., 2007) were employed for the removal of dyes, color and trace elements from waste water. Coir pith carbon was found to be useful adsorbent for the removal of Congo red (Namasivayam and Kavitha, 2002). Moreover, many Ligno-cellulosic materials such as banana pith (Namasivayam et al., 1993), coir pith (Namasivayam and Kadirvelu, 1994), eucalyptus bark (Morais et al., 1999), apple pumice and wheat straw (Robinson et al., 2002),

*Corresponding author. E-mail: rashid_meh786@yahoo.com.

rice husk (Vadivelan and Kumar, 2005), pine sawdust (Ozacar and Engil, 2005), peanut hull (Gong et al., 2005), lemon peel (Kumar and Kumaran, 2005), almond shell (Ardejani et al., 2008), neem leaf powder (Tahir et al., 2008) and animal bone meal (Mohammadine, 2012) were also used for the removal of dyes from water.

In the present study the cow dung ash has been used for the removal of EBT from aqueous solution through simple batch technique. The investigations were carried out by varying contact time from 10 to 120 min and concentration of adsorbate from 2 to 10 mgL^{-1} and adsorbent dosage of 1 g at 303 and 308K and pH = 7. The data was employed to the Langmuir and Freundlich adsorption isotherms to determine their constants. Thermodynamic parameters such as free energy, enthalpy and entropy were also calculated.

Molecular structure and molecular formula of Erichrome Black T (EBT)



IUPAC names

Sodium (4z)-4-[(1-hydroxynaphthalen-2-yl-hydrazinylidene-7-nitro-3-oxo Y-nephthalen-1-sulfonate.

Systematic names

Sodium 4-[2-(1-hydroxynaphthalen-2-yl) hydrazin-1-ylidene]-7-nitro-3-oxo-3,4 dihydronaphthalene-1-sulfonate.

Molecular formula: $C_{20}H_{12}N_3O_7SNA$

EBT is a complexometric indicator that is part of the complexometric titrations, e.g. In the water hardness determination process. It is an azo dye. In its protonated form, EBT is blue. It turns red when it forms a complex with calcium, magnesium, or other metal ions. Its chemical formula can be written as $HOC_{10}H_6N{=}NC_{10}H_4$ (OH) (NO_2) SO_3Na.

MATERIALS AND METHODS

Adsorption studies were carried out using batch method. EBT (95.5%) supplied by fluka was used without any further purification. The cow dung ash used in the present work was obtained by firing the animal waste in open air and then dried at 105°C for 24 h to remove the moisture and stored in desiccator for further use in the adsorption studies. The stock solution of EBT was prepared by dissolving 10 mg of EBT in distilled water to make 1000 ml of the solution. It was further diluted to the required initial concentrations 8, 6, 4 and 2 mg/L, respectively. The wavelength for maximum absorption (λ_{max}) was determined using spectrophotometer (VIS-1100 (BMS) and it was found to be 623 nm. Absorption of the given solutions was measured at λ_{max}, and calibration curve was drawn to determine the molar absorption co-efficient. The 1 g of adsorbent was added in 100 ml of each dye solution and agitated at 150 rpm for 10 to 120 min in electrical shaking water bath DFD-700 (Glas-Col) at 303 and 308K, respectively. After shaking the samples for given time, their pH was maintained with 0.1 M NaOH and/or 0.1 M HCl using pH-meter pH-720 (Ino LAB). The samples were immediately filtered using Whatmann filter paper (No. 43) and analyzed through spectrophotometer to determine the concentration of each EBT solution after adsorption using Beer's Lambert law. The dye uptake was determined by employing the following mass balance equation.

$$q_e = (C_i-C_e)\ V / M \tag{1}$$

Where V is the volume of solution (L), M is the mass of the adsorbent used (g) and Ci and C_e are the initial and equilibrium concentrations (mg/L) of the dye, respectively. The removal efficiency or percent adsorption was calculated using the following equation

$$\text{Removal efficiency} = (Ci - Ce/Ci) \times 100 \tag{2}$$

RESULTS AND DISCUSSION

Effect of contact time

Figures 1 and 2 show the effect of shaking time on the adsorption capacity of EBT at 303 and 308 K, respectively. The results reveal that adsorption increases with increase in agitation time and reaches equilibrium after 60 min for each concentration from (2 to 10 mg/L) for 1 g adsorbent at both temperatures. The results indicate that the removal efficiency for 2 mg/L solution and 1 g adsorbent reaches up to 57.15% and then for 4, 6 and 8 ppm, it reaches to 83.03, 90.40 and 93.73%, respectively after the shaking of initial 10 min. Data also reveal that rate of removal efficiency decreases with increase in shaking time from (10 to 60 min). The increase rate of sorption of the dye in the initial period of the process may be due to higher number of sites available on the surface of the adsorbent and the higher concentration gradient between the adsorbate in the solution and adsorbate on the surface of the adsorbent. As the uptake of the dye progresses the concentration gradient between the dye in the solution and dye on the surface of the adsorbent decreases and the number of vacant adsorption sites on the adsorbent surface also

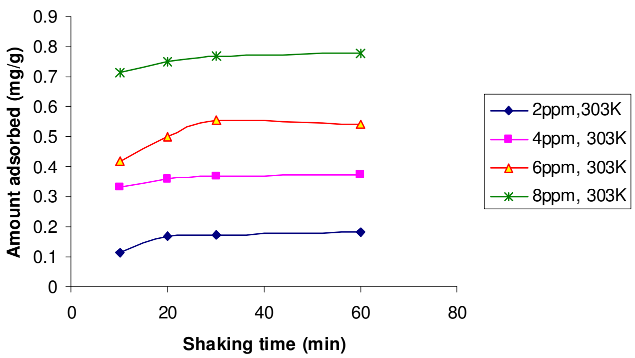


Figure 1. Effect of shaking time on adsorption of EBT onto1 g of cow dung ash at 303 K and pH 7.

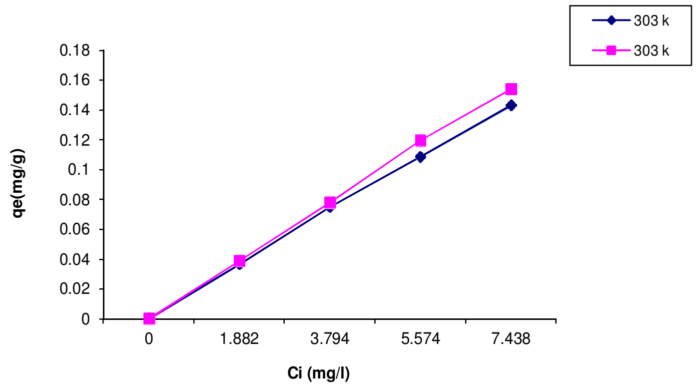


Figure 3. Effect of dye concentration on adsorption over cow dung at 303 and 308K.

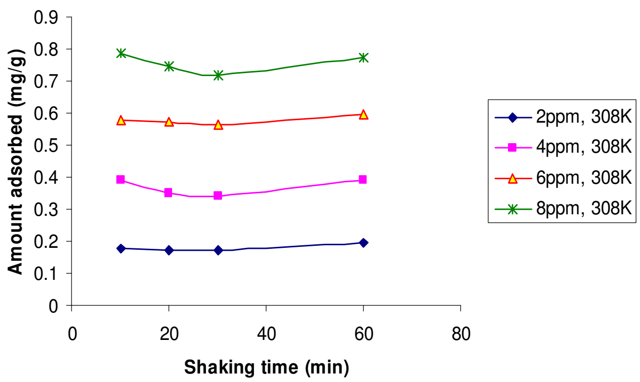


Figure 2. Effect of shaking time on adsorption of EBT onto1 g of cow dung ash at 308 K and pH 7.

decreases leading to a decrease in adsorption rate with time. The maximum removal efficiency was found to be 97.41% for 8 mg/L solution after the shaking of 60 min.

Effect of initial concentration

Figure 3 shows the effect of initial concentration of EBT on its adsorption on cow dung ash from aqueous solution at 303 and 308K. The data reveals that adsorption starts at low concentration and increases with increase in the concentration of adsorbate at both temperatures. The adsorption capacity of EBT was found to increase from 0 .20 to 0.75 and 0.2 to 0.8 mg/g with 1 g of adsorbent at 303 and 308K, respectively by increasing concentration from 2 to 10 mg/L.

Adsorption isotherms

An adsorption isotherm is characterized by certain constants, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorption capacities of the adsorbent for different adsorbate. The equilibrium data owing to the dependence of the adsorption of initial dye concentration is best studied by the Langmuir and Freundlic isotherms. A linearized form of Langmuir equation is as follows

$$1/q_e = 1/Q_o + 1/Q_oK_L. 1/Ce \qquad (3)$$

A plot of 1/qe versus 1/Ce was found to be a straight line with $1/Q_o$ as intercept and $1/Q_o K_L$ as slope and hence Q_o and K_L can be calculated. The linearized form of the Freundilch equation can be written as:

$$Inq_e = In K_F + 1/n InC_e \qquad (4)$$

A plot of Inq_e versus InC_e gives a straight line and K_F and n can be calculated from the intercept and slope, respectively. Figures 4 and 5 show the Langmuir adsorption isotherms and Figures 6 and 7 show the Freundlich adsorption isotherms of EBT at 303 and 308K, respectively. The Langmuir constants K_L and Q_o and Freundlich constants n and K_F and the correlation co-efficient R^2 are given in Table 1. As suggested by some workers (Namasivayam and Yamuna, 1992; Raji and Anirudhan, 1998) if the value of Freundlich constant n is such that 0.1 < n < 1, the adsorption is favorable. This shows the effectiveness of cow dung ash for the removal of EBT from aqueous solutions. However, the linearized equation did not give a good correlation for the removal of EBT onto cow dung ash, indicating that EBT adsorption by cow dung fits better to the Langmuir model than to the Freundlich model. In the present study the values of n lie in this suggested range. Similarly, a dimensionless constant R_L, called separation factor can be defined from the Langmuir constant K_L (Hall et al., 1966) is as follows:

$$R_L = 1/ (1+ C_i K_L) \qquad (5)$$

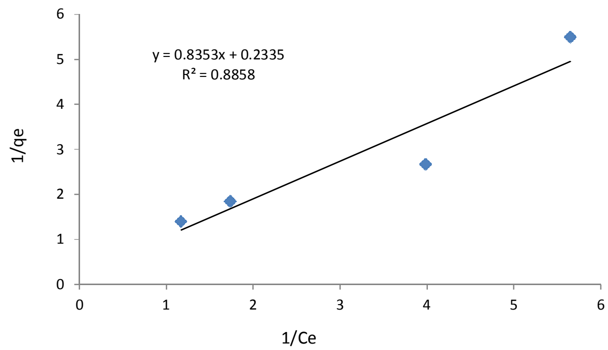


Figure 4. Langmuir adsorption isotherm of adsorption of EBT over cow dung at 303K(adsorbent dose 1g, pH = 7).

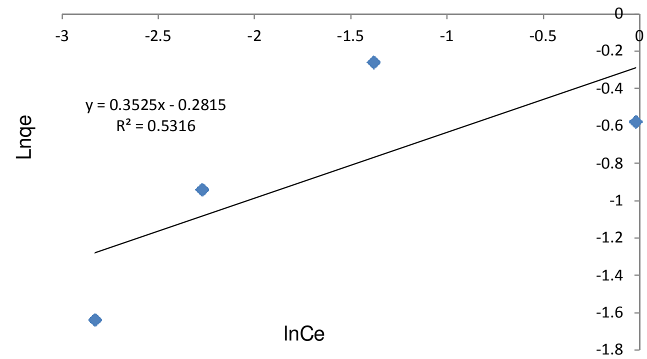


Figure 7. Freundlich adsorption isotherm for adsorption EBT over cow dung at 308K.

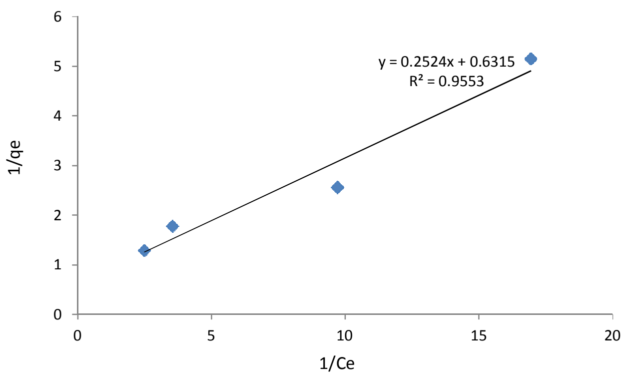


Figure 5. Langmuir adsorption isotherm of adsorption of EBT over cow dung at 308K (adsorbent dose 1 g, pH = 7).

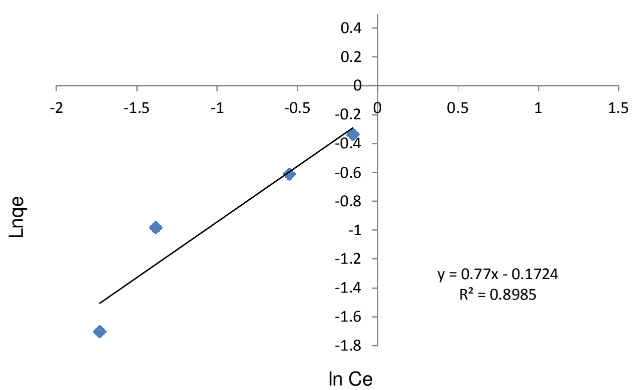


Figure 6. Freundlich adsorption isotherm for adsorption EBT over cow dung at 303K.

Where C_i is the initial concentration of the EBT solution. According to McKay et al. (1982) for favorable adsorption $0 < R_L < 1$, and for unfavorable adsorption $R_L > 1$ and RL = 1 represents linear absorption while $R_L = 0$ represents irreversible adsorption process. As seen in Table 3, for all initial concentrations the value of R_L falls in the range of 0 and 1 showing the favorable adsorption of EBT on cow dung ash from aqueous solution at 303 and 308K, respectively.

Thermodynamic parameters

Thermodynamic parameters such as free energy, enthalpy and entropy changes associated with the adsorption of EBT on the cow dung ash were determined from the binding energy constant K_L obtained from Langmuir equation by using the following equations:

$$\Delta G = - RT \ln K_L$$

$$- RT \ln K_L = \Delta H - T \Delta S$$

$$\ln K_L = (- \Delta H/RT) + (\Delta S/R)$$

$$\ln K_{L1} = (- \Delta H/RT_1) + (\Delta S/R)$$

$$\ln K_{L2} = (- \Delta H/RT_2) + (\Delta S/R)$$

$$\ln K_{L2} - \ln K_{L1} = (\Delta H/RT_1) - (\Delta H/RT_2)$$

$$\ln (K_{L2}/ K_{L1}) = \Delta H/R (1/T_1 - 1/T_2) \quad (6)$$

$$\Delta H = (RT_1T_2/ T_2-T_1) \ln (K_{L2}/ K_{L1}) \quad (7)$$

Where, K_{L1} and K_{L2} are the Langmuir binding constants at T_1 (303K) and T_2 (308K), respectively. By putting the values of ΔG and ΔH into the following equation the entropy of adsorption at T_1 and T_2 can be calculated.

$$(\Delta S) = (\Delta H-(\Delta G) /T)$$

$$(\Delta S)_1= (\Delta H-(\Delta G)_1/T_1)$$

$$(\Delta S)_2= (\Delta H-(\Delta G)_2/T_2) \quad (8)$$

Table 1. Freundlic and Langmuir parameters for adsorption of Eriochrome Black-T over cow dung at different temperatures.

Temperature (K)	n	log K_F	R^2	Q_o (mol/g)	K_L(L/mol)	R^2
303	1.299	-0.172	0.898	4.292	0.280	0.885
308	2.841	-0.281	0.531	1.585	2.504	0.955

Table 2. Values of thermodynamic parameters for adsorption of Eriochrome Black-T over cow dung.

Temperature (K)	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o(k J $K^{-1}mol^{1}$)	Ea (kJ mol^{-1})
303	3.206	326.328	1.063	326.28
308	-2.351	-	1.698	-

Table 3. Separation factor R_L calculated from Langmuir parameter K_L at various initial concentrations of EBT at different temperatures.

Temperature (K)	Mass of adsorbent (g)	K_L	Initial concentration (mg/L)	R_L
303	1	0.280	2	0.64
			4	0.47
			6	0.37
			8	0.31
308	1	2.504	2	0.164
			4	0.091
			6	0.063
			8	0.050

The value of ΔG was calculated using Equation (6), where R is the gas constant (8.314 $JK^{-1}mol^{-1}$). The values of ΔS were calculated using Equation (8). These values are tabulated in Table 2. The value of ΔG was found to be negative at 308K that showed the adsorption was spontaneous at this temperature. The activation energy Ea was calculated using the following equation:

$$Ea = R\,(T_1T_2/T_2\text{-}T_1)\ \ln K_2/K_1 \quad (9)$$

Conclusions

Cow dung ash was found to a useful waste biomass adsorbent for the removal of EBT from aqueous solution. Adsorption capacity was found to increase with increase in initial concentration. Data employed to both Langmuir and Freundlich adsorption isotherms were found to be well fitted to the Langmuir adsorption isotherm. The adsorption of EBT was found to be endothermic and spontaneous especially at 308K.

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