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Sorption of basic dyes from aqueous solution by activated sludge

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Abstract

The adsorption of dyes in the solutions using activated sludge might be a promising approach in wastewater treatment units. The adsorption of Basic Red 18 and Basic Blue 9 from aqueous solution by dried activated sludge was investigated with in a batch system. The activated sludge had the highest dye uptake capacity, having the monolayer adsorption capacity 285.71 and 256.41 mg g^{-1} for Basic Red 18 and Basic Blue 9, respectively, at pH value of 7.0 and 20 °C. Langmuir and Freundlich adsorption models were used for the mathematical description of the adsorption equilibrium and the equilibrium data fixed very well with both the Langmuir and Freundlich models. The R_L values showed that, activated sludge was favorable for the adsorption of basic dyes. The suitability of the kinetic models for the adsorption of dyes on the activated sludge was also discussed. It was clear that the adsorption kinetics of dyes to dried activated sludge obeyed pseudo second-order adsorption kinetics.

Keywords: Adsorption; Activated sludge; Basic Blue 9; Basic Red 18; Kinetic

1. Introduction

Synthetic dyes are used extensively by industries including dyehouses, paper printers and textile dyers. A significant proportion of synthetic organic dye stuffs are lost annually to waste streams in textile processing, which eventually enter the environment [1]. Colour is usually the first contaminant to be considered in wastewater. Its presence in watercourses is unacceptable. A very small amount of dye in water is (10–50 mg l^{-1}) highly visible and effects water transparency and gas solubility of water bodies [2]. Moreover, it may also affect photosynthetic activity in aquatic systems by reducing light penetration [3,4]. Several commonly used dyes have been reported to be carcinogenic and mutagenic for aquatic organisms [5].

The removal of textile dyes from wastewater is one of the most important environmental issues to be solved today. Many dyes used in textile industry are particularly difficult to remove by conventional waste treatment methods since they are designed to be resistant to degradation or fading by oxidizing agents and light. They must also be resilient to both high temperatures and enzyme degradation resulting from detergent washing. For these reasons, biodegradation of these dyes is typically a slow process and complete mineralization of most dyes is rather difficult. Degradation products are toxic and carcinogenic amines to aquatic organisms [6–8]. Their presence in wastewater is unwanted and the removal of such compounds are difficult while many physical and chemical methods including adsorption, coagulation, precipitation, filtration, ozonation and oxidation have been used for the treatment of dye-containing effluent [2–9]. Activated carbon is the most widely used adsorbent for the removal of colour and treatment textile effluents. However, due to its high price, it is not used on a great scale [3]. This had led many workers to search for the use of cheap and efficient alternative materials such as bagasse pith, carbonized bark, peat, soil, tree and Eucalyptus bark, chitin, rice husk wood and fly ash [3,9–13]. The activated sludge process, being the most commonly used in biological wastewater treatment methods, is the most abundant source of microbial biomass.

The objective of this study was to determine the dye uptake characteristics of activated sludge for a number of commercially used basic dyes in aqueous solution.

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2. Materials and methods

2.1. Adsorbate and adsorbent

Activated sludge biomass, as an adsorbent, was collected from Adana Organize Sanayi full scale wastewater treatment system, Adana, Turkey. Basic Blue 9 (BB 9) and Basic Red 18 (BR 18) were used as adsorbates in this study, which were purchased from Aldrich. The chemical structures of BR 18 and BB 9 are shown in Fig. 1.

2.2. Preparation of biomass for adsorption

Activated sludge biomass was prepared according to methods described by Aksu [12]. Activated sludge biomass was harvested by centrifugation and washed twice with in distilled water and than dried at 60 °C until constant weight. A weighed amount of dried activated sludge was suspended in distilled water and homogenized in homogenizer (Janke and Kunkel, IKA-Labortechnick, Ultra Turrax T25) at 8000 rpm for 20 min and then stored in a refrigerator for adsorption studies. The concentration of stock biomass solution was 10 g l^{-1}.

2.3. Adsorption studies

Adsorption studies [32,33] were conducted in 250 ml Erlenmeyer flasks using 100 ml of biomass–synthetic dye solutions. A known concentration of 90 ml dye solution was added to 10 ml activated sludge biomass suspension in Erlenmeyer flask at the temperatures and pH values studied. The flasks were agitated on a shaker at 150 rpm. Samples were taken at pre determined time intervals (0, 5, 10, 20, 40, 60, 80, 120, 150, 210 and 300 min) for the analysis of residual dye concentration in solution. The dye biomass mixtures were centrifuged at 4000 rpm for 5 min and than the supernatant liquid was analyzed for the remaining dye.

2.4. Analysis

The concentration of dye in the sample solution was determined spectrophotometrically (Shimadzu 2001 UV Spectrophotometer) at 668 and 640 nm wavelengths for BR 18 and BB 9, respectively.

Adsorbed dye amount by activated sludge was calculated using Eq. (1)

$$q_e = \frac{(C_0 - C_t)v}{W} \quad (1)$$

where q_e is the amount-adsorbed dye, C_0 the initial dye concentration, C_t the equilibrium dye concentration in solution at time t, v the solution volume, and W is the adsorbent weight. All experiments were carried out in triplicate. Adsorbed dye concentrations were the means of the three replicates.

The average percentage errors between the experimental and predicted values were calculated using Eq. (2).

$$\varepsilon(\%) = \frac{\sum_{i=1}^{N} |[(q_e, i)_{cal} - (q_e, i)_{exp}]/(q_e, i)_{exp}|}{N} \times 100 \quad (2)$$

where exp and cal show the experimental and calculated values of q_e and N is the number of measurements.

3. Results and discussion

3.1. Effect of pH

The pH value of the solution was an important parameter for controlling the adsorption process [14]. Effect of pH on adsorption was studied at 100 mg l^{-1} dye concentration at 20 °C between pH values 2 and 10. Effect of pH variation on equilibrium uptake is given in Fig. 2. The adsorption of BR 18 and BB 9 increased with pH up to 6–10. Similar results were shown by various authors [11,13,15]. Adsorptions of two basic dyes at pH 7 were 73.6 and 61.3 mg g^{-1} for BR 18 and BB 9, respectively. Solution pH was shown to influence both cell surface dye binding sites and dye chemistry in water [14]. Negatively charged adsorbent sites decreased with decreasing hydrogen ion concentration while number of positively charged surface sites increased, which did not favour the adsorption of positively charged dye cations [15,16].

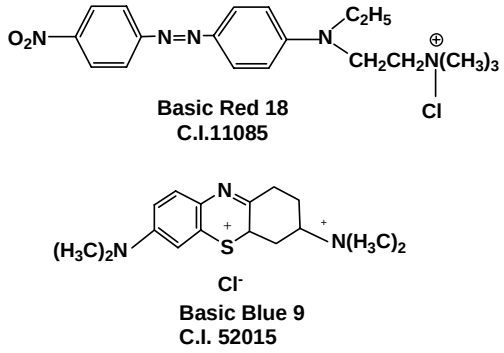

Fig. 1. Chemical structures of BR 18 and BB 9.

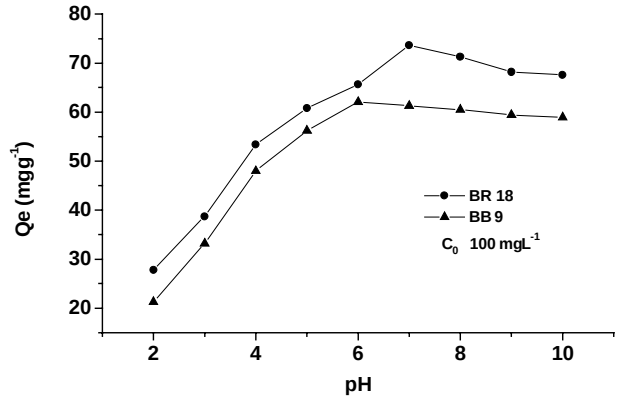

Fig. 2. Effect of pH on adsorption.

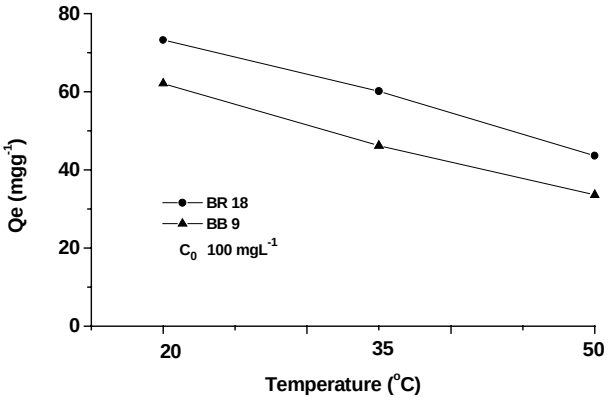

Fig. 3. Effect of temperature on adsorption.

3.2. Effect of initial temperature on adsorption

Temperature influenced the dye adsorption properties of activated sludge. The effect of initial temperatures on equilibrium uptake is given in Fig. 3. Temperature effect on biosorption capacity of dried activated sludge was studied at 20, 35 and 50 °C using 100 mg l^{-1} initial dye concentrations at pH 7.0. Adsorption capacities of dried activated sludge increased with decreasing temperatures from 50 to 20 °C which indicated that the adsorption process was exothermic [17]. The sorption capacity of dried activated sludge were determined as 73.2, 60.1 and 43.6 mg g^{-1} for BR 18 and 61.2, 46.2 and 33.6 mg g^{-1} for BB 9 at 20, 35 and 50 °C, respectively. The optimum temperature for dye adsorption of activated sludge was found to the 20 °C within the temperature range studied.

3.3. Effect of contact time and concentration

The adsorption of basic dyes at affixed concentration on activated sludge was studied as a function of contact time to determine the equilibrium time (Fig. 4). Nearly 45 min were required for the equilibrium adsorption for both basic dyes. Therefore, equilibrium time was set conservatively at 300 min for further experiments. Adsorption of both basic dyes was very fast initially and nearly 50% of dyes were adsorbed in less than 5 min. The equilibrium states were attained in 40 min for 25 and 50 mg l^{-1} and in 60 min for 100 mg l^{-1} initial dye concentrations. Equilibrium dye uptakes of activated sludge were determined as 22.3, 39.4 and 73.5 mg g^{-1} for BR 18 and 19.5, 29.4 and 62.9 mg g^{-1} for BB 9 at 25, 50 and 100 mg l^{-1} initial dye concentrations, respectively. Adsorption capacities of dried activated sludge increased with increasing the initial dye concentration. This is due to increase in the driving force of the concentration gradient, as an increase in the initial dye concentration.

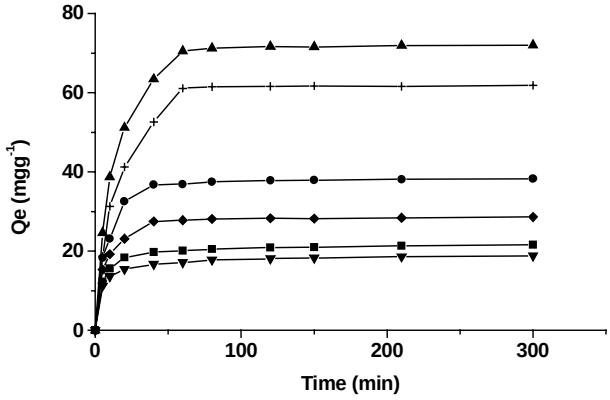

Fig. 4. The initial sorption tests of BR 18 (▲, ●, ■) and BB 9 (+, ◆, ▼) for 100, 50 and 25 mg l^{-1} dye concentration, respectively.

The initial dye concentration influenced the adsorption time of dyes on dried activated sludge. Effect of initial concentration on adsorption time was consisted with the observations Benguella and Benaissa [18] for sorption of cadmium by chitin, Low et al. [19,20] for the adsorption of basic dyes by water hyacinth roots and by *Hydrilla verticillata* and of Waranusantigual et al. [14] for the sorption of methylene blue by *Spirodela polyrrhiza*. The equilibrium uptake was reached very rapidly for the dye concentrations less than 100 mg l^{-1}, generally less than 10 min [14,19,20]. They suggested that the rapid uptake of dyes indicate that the sorption process could be ion-exchange in nature where the cationic dye molecules bind with the various negatively charged organic functional groups present on the surface of the biomass.

3.4. Adsorption isotherm

The Langmuir [21]and Freundlich [22] adsorption isotherm models were used to describe the biosorption equilibrium. The linearized equation of Langmuir is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (3)$$

where q_e is adsorbed dye at equilibrium (mg g^{-1}), C_e the equilibrium concentration of dye in solution after adsorption (mg l^{-1}) and a_L (l mg^{-1}) and K_L (l g^{-1}) are the Langmuir constants which are calculated by plotting of C_e/q_e versus C_e. The slope and intercept of the line is a_L/K_L and $1/K_L$, respectively. The theoretical monolayer capacity (q_{max}) are numerically equal to K_L/a_L.

The essential features of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L which was defined by McKay et al. [23] as

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

where K_L is the Langmuir isotherm constant and C_0 is the initial dye concentration (mg l^{-1}). The value of R_L indicates the shape of the isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Table 1
Langmuir and Freundlich isotherm constant of BR 18 and BB 9

Dye	Langmuir						Freundlich		
	Temperature (°C)	$a_L \times 10^{-2}$	K_L	R^2	q_{max}	$R_L \times 10^{-2}$	K_F	$1/n$	R^2
BR 18	20	1.32	3.782	0.996	285.71	0.044	8.785	0.5932	0.976
	35	0.69	1.865	0.984	270.27	0.089	5.248	0.6599	0.992
	50	0.56	1.032	0.989	181.81	0.161	2.030	0.7334	0.997
BB 9	20	0.894	2.294	0.994	256.41	0.073	5.287	06421	0.971
	35	0.596	1.242	0.985	208.33	0.134	3.268	0.6496	0.984
	50	0.482	0.831	0.981	172.40	0.200	2.152	0.6670	0.981

R^2, correlation coefficient.

The most important multi-site adsorption isotherm for heterogeneous surfaces is the Freundlich adsorption isotherm:

$$q_e = K_F C_e^{1/n} \quad (5)$$

Eq. (5) can be linearized by taking logarithms to find out the parameters K_F and n.

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (6)$$

where K_F is the Freundlich constant, n the Freundlich exponent, q_e the amount of adsorbed dye at equilibrium (mg g^{-1}), and C_e is the equilibrium concentration of dye in solution after adsorption (mg l^{-1}).

The adsorption isotherms were studied at 20, 35 and 50 °C. A plot of linear Langmuir equation C_e/q_e versus C_e is shown in Fig. 5. The value of isotherm constants, a_L, K_L and equilibrium monolayer capacities, q_{max}, are given in Table 1. The monolayer capacities of activated sludge increased with decreasing temperatures and were determined as 285.71, 270.27 and 181.81 mg g^{-1} for BR 18 and 256.41, 208.33 and 172.4 mg g^{-1} for BB 9, at 20, 35 and 50 °C, respectively.

The R_L values given in Table 1, showed that the adsorption behaviour of activated sludge were extremely favorable for the two basic dyes ($R_L < 1$). The low values of R_L indicated that adsorption tend to be weakly irreversible ($R_L = 0$).

Plots of logarithmic Freundlich expression and isotherm constants were given in Fig. 6 and Table 1, respectively. High correlation coefficient ($R^2 > 0.98$) and the magnitude of exponent n indicated the favorability and the capacity of the adsorbent/adsorbate system. The values of n was $1 < n < 10$ which indicated that adsorption is good [12].

3.5. Adsorption kinetics

A study of adsorption kinetics is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process. Successful application of the adsorption demands innovation of cheap, easily available and abundant adsorbents of known kinetic parameters and sorption characteristics. Thus, the effects of some parameters on adsorption were investigated, such as contact time, initial dye concentration, solution pH and temperature [18,24–26]. The adsorption results of BR 18 and BB 9 show that 20 °C and neutral pH value was suitable for good adsorption. Thus, effect of initial dye concentration on adsorption kinetics had been studied at 20 °C and pH 7.0. Adsorption kinetics can be modeled by the pseudo first-order Lagergren equation [27], second-order equation [28] and pseudo second-order rate equation [29] given below as Eqs. (7)–(9), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (7)$$

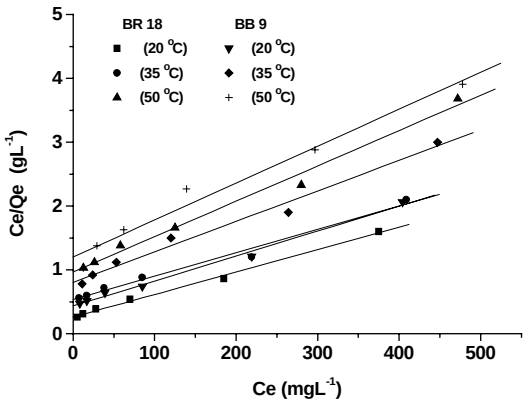

Fig. 5. Linear Langmuir isotherm plots of BR 18 and BB 9.

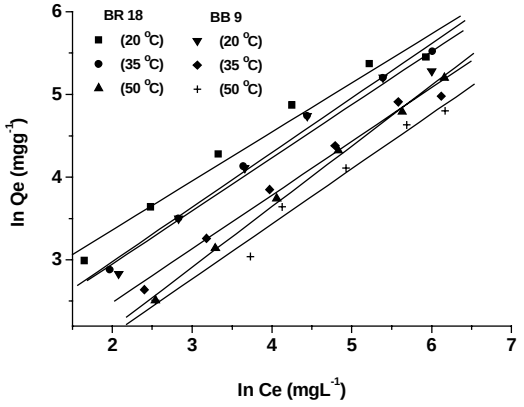

Fig. 6. Linear Freundlich isotherm plots of BR 18 and BB 9.

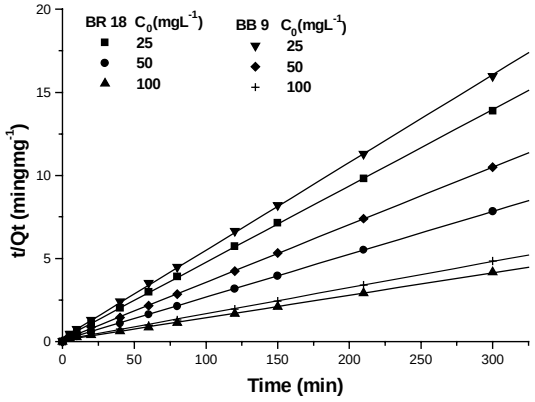

Fig. 7. Pseudo second-order sorption kinetics of BR 18 and BB 9.

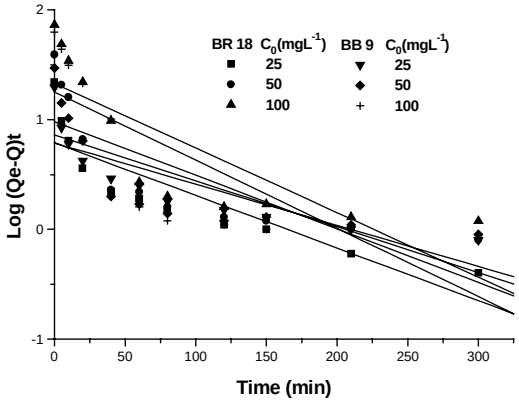

Fig. 8. Pseudo first-order sorption kinetics of BR 18 and BB 9.

$$\frac{1}{q_e - q_t} = \frac{1}{q_e^2} + K_2 t \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{K_3 q_e^2} + \frac{1}{q_e} t \quad (9)$$

where K_1 is the rate constant of pseudo first-order adsorption (min^{-1}), K_2 (g mg^{-1} min) the rate constant of second-order adsorption and K_3 (g mg^{-1} min) the rate constant of pseudo second-order adsorption, q_e and q_t are amount of dye adsorbed on adsorbent (mg g^{-1}) at equilibrium and at time t, respectively.

Linear plots of t/q_t versus t, $\log(q_e - q_t)$ versus t and $1/(q_e - q_t)$ versus t and the adsorption kinetic rate constants are shown in Figs. 7–9 and Table 2, respectively.

If pseudo second-order kinetic applicable, the plot of t/q_t versus t should show a linear relationship. There is no need to know any parameter before and q_e and K_2 can be determined from the slope and intercept of the plot [18,30]. The pseudo second-order reaction rate model adequately described the kinetics of sorption of basic dyes with high correlation coefficient ($R^2 > 0.999$) in Fig. 7, and its calculated equilibrium capacities ($q_{e\,cal}$) fit well the experimental data. The values of these parameter and percentage errors (ε (%)) were given in Table 2. These suggested that the pseudo second-order

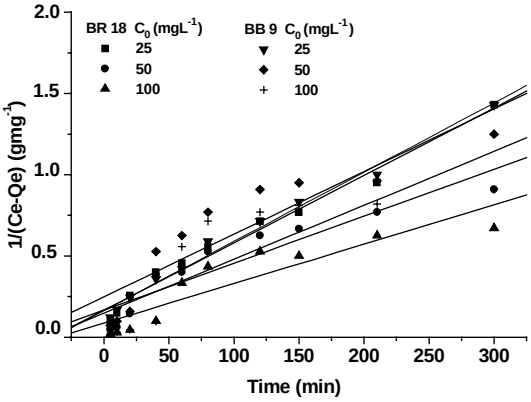

Fig. 9. Second-order sorption kinetics of BR 18 and BB 9.

Table 2
Comparison of the kinetic rate constants

Basic Red 18						Basic Blue 9				
C_0	$q_{e\,exp}$	$q_{e\,cal}$	ε (%)	K_1 ($\times 10^{-2}$)	R^2	$q_{e\,exp}$	$q_{e\,cal}$	ε (%)	K_1 ($\times 10^{-2}$)	R^2
Pseudo first-order kinetic model										
25	22.3	6.14	72.46	1.100	0.768	19.5	6.16	68.41	0.852	0.724
50	39.4	9.60	75.63	1.128	0.631	29.4	7.90	73.13	0.967	0.582
100	73.5	21.5	70.74	1.359	0.664	62.9	19.9	68.36	1.428	0.623
C_0	$q_{e\,exp}$	$q_{e\,cal}$	ε (%)	K_2 ($\times 10^{-2}$)	R^2	$q_{e\,exp}$	$q_{e\,cal}$	ε (%)	K_2 ($\times 10^{-2}$)	R^2
Second-order kinetic model										
25	22.3	6.459	71.07	0.42	0.978	19.5	6.138	68.52	0.43	0.987
50	39.4	6.038	84.69	0.29	0.869	29.4	4.029	86.32	0.39	0.830
100	73.5	11.49	84.36	0.24	0.820	62.9	6.780	89.22	0.33	0.714
C_0	$q_{e\,exp}$	$q_{e\,cal}$	ε (%)	K_3 ($\times 10^{-2}$)	R^2	$q_{e\,exp}$	$q_{e\,cal}$	ε (%)	K_3 ($\times 10^{-2}$)	R^2
Pseudo second-order kinetic model										
25	22.3	21.7	2.69	1.24	1	19.5	18.9	3.07	1.3	1
50	39.4	38.7	1.77	0.75	1	29.4	28.9	1.70	1.1	1
100	73.5	74.4	1.22	0.24	0.999	62.9	63.6	1.11	0.2	0.999

R^2, correlation coefficient.

adsorption mechanism was pre dominant and that the overall rate of the dye adsorption process appeared to be controlled by chemical process [30,31]. The results indicated that for the pseudo second-order model, where rate constant decreased with increasing initial dye concentration, and the initial adsorption rate increased with increasing initial dye concentration [18].

The pseudo first-order and second-order kinetic models did not show a good correlation ($R^2 < 0.900$) as shown in Table 2. The calculated values of q_e form the pseudo first-order and second-order kinetic models were lower than the experimental ones. The results showed that the sorption of BR 18 and BB 9 by the activated sludge were not suitable for the pseudo first-order and second-order models.

4. Conclusion

In batch adsorption studies, data showed that dried activated sludge had considerable potential for the removal of basic dyes (BR 18 and BB 9) form aqueous solution. Langmuir and Freundlich isotherms were fitted very well with studied temperature and concentration ranges. The R_L values showed that activated sludge was favorable for the adsorption of basic dyes.

The suitability of the kinetic models for the adsorption of dyes on the activated sludge was also discussed. It was clear that the adsorption kinetics of dyes to dried activated sludge obeyed second-order adsorption kinetics.

It may be concluded that dried activated sludge may be used for elimination of textile dyes from wastewater. Activated sludge is a low cost natural abundant adsorbent material and it may be alternative to more costly adsorbent materials.

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