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Biosorption of Basic Dyes Using Sewage Treatment Plant Biosolids

Md. Zahangir Alam
Department of Biotechnology Engineering, Faculty of Engineering,
International Islamic University Malaysia, Jalan Gombak, 53100 Kuala Lumpur, Malaysia

Abstract: Studies on the removal of three basic dyes (Basic Blue 3, Basic Red 22, Basic Black 9) from aqueous solutions by adsorption on Sewage Treatment Plant (STP) biosolids (sludge) as an adsorbent were carried out with an aim to obtain information on treating effluents from textile and/or dye industries. A series of experiments were undertaken in a batch adsorption technique to access the effect of the process variables i.e. initial dye concentration, contact time, initial pH, adsorbent dose, temperature and agitation rate. The adsorption capacity of basic dyes was higher (22-24 mg g^{-1}) with the lower values of the temperature (25-30°C), adsorbent dosage (0.5-0.75% w/v), higher values of the initial pH (8-9) and agitation rate (150-200 rpm). The equilibrium in the solution was observed within 2 h of operation. The equilibrium isotherm for each dye was determined to describe the biosorption processes. The results showed that the equilibrium data were fitted by both of the Langmuir and Freundlich isotherms while Freundlich isotherms was slightly better fitted for Basic Blue 3 and Langmuir was for the Basic Black 9 in terms of regression coefficients (R^2).

Key words: Sewage Treatment Plant (STP) biosolids, biosorption, basic dyes, adsorption isotherm, low-cost adsorbent

INTRODUCTION

Among various industries, textile industry ranks first in usage of dyes for coloration of fiber. Today more than 9000 types of dyes have been incorporated in the color index[1]. Due to low biodegradability of dyes, a conventional biological treatment process is not very effective in treating a dye wastewater. Many physical and chemical methods including coagulation, precipitation, filtration, oxidation, membranes have been used for the treatment of dye-containing effluents[2-5]. However these processes are costly and cannot effectively be used to treat the wide range of dye waste waters.

Adsorption processes have been investigated as an efficient and effective method to remove dyes from wastewater. The most widely used adsorbent for industrial applications is activated carbon[6,7]. There are still problems associated with its use namely activated carbon is expensive and the higher the quality the greater the cost. Due to its higher cost and considering the large quantity of wastewater normally produced by the textile industries, research has recently been focused towards alternative adsorbents namely low cost adsorbents including the utilization of waste materials capable of removing significant quantities of dyes from aqueous solutions[1,8-11].

A waste material such as Sewage Treatment Plant (STP) biosolids (sludge) would be unlikely to possess as high as adsorption capacity as a commercial adsorbent such as activated carbon[10,12,13]. It will be considerably cheaper and is a great headache for sludge management to its safe and environmental-friendly disposal. This potentially offers a more economic approach to the removal of basic dyes using STP biosolids as an effective adsorbent. The aim of this study was to determine the adsorption capacity of STP biosolids in aqueous solutions varying with process factors include initial dye concentration, contact time, initial pH, adsorbent dose, temperature and agitation rate.

MATERIALS AND METHODS

Sample collection: The Sewage Treatment Plant (STP) biosolids (sludge) used as an adsorbent was obtained from a sand drying bed which is coming from secondary clarifier in the Indah Water Korsortium (IWK) sewage treatment plant, Kuala Lumpur, Malaysia. The sample was containing 7-10% (w/w) of Total Suspended Solids (TSS) with the initial pH of 6.2. After removal of excess water the solids were dried at 103°C in an oven until of its constant weight, ground with a steel bender, sieved into a discrete

Corresponding Author: Md. Zahangir Alam, Bioenvironmental Engineering Research Group,
Department of Biotechnology Engineering, Faculty of Engineering,
International Islamic University Malaysia, Jalan Gombak, 53100 Kuala Lumpur, Malaysia
Fax: +603-20564442 Tel: +603-20564571 E-mail: zahangir@iiu.edu.my

particle size ranges of 125-150 μm. The ready sample was stored in a desiccator for adsorption experiment. The three basic dyes were used for this study. The dyes were: Basic Blue 3 (BD-Blue), Basic Red 22 (BD-Red) and Basic Black 9 (BD-Black). All dyes used as an adsorbate were supplied by Merck and Co. (Germany). The dye samples were stored at 4°C until used.

Batch adsorption experiments and analysis: The batch adsorption experiments were conducted in a laboratory by contacting a specific volume of basic dye (adsorbate) with the same quantity of STP biosolids as an adsorbent. A stock solution of basic dyes with a concentration of 1000 mg L^{-1} was prepared, dilutes it for adsorption experiment as per experimental conditions. Measured quantity of adsorbent (0.2-0.75 g) were placed to the 250 mL of conical flask to which a measured 50 mL of dye solution with the concentration of 50-300 mg L^{-1} was added. The samples were reciprocated in a rotary shaker at 30±2°C with a controlled agitation (50-400 rpm) for 48 h in order to investigate the equilibrium of the adsorption process. The samples were then centrifuged and the residual concentration of dyes solution was determined using a UV spectrophotometer (UVICON 333). All measurements were performed at the wavelength of 660 nm using distilled water as a blank. The removal rate was calculated comparing with the control which was followed same procedures without having adsorbent.

The adsorption capacity q_e was calculated from the difference between the initial and equilibrium adsorbate (dye) concentration which is as follows:

$$q_e = \frac{(C_o - C_e)}{M} V \qquad (1)$$

where, q_e is the adsorption capacity (mg g^{-1}), C_o and C_e are the initial and equilibrium concentration (mg L^{-1}) respectively, M is the adsorbent dosage (g) and V is the solution volume (L).

Table 1: Biosorption of basic dyes with deferent process conditions

Process factors	Other conditions
Contact time 0.25, 0.5, 0.75, 1, 2, 3, 4, 5, 6, 12, 18, 24, 48 (h)	Temperature: 30°C, agitation: 150 rpm; adsorbent dose: 0.2 g; initial pH: 7
Initial pH 3, 4, 5, 6, 7, 8, 9	Contact time: 2 h; Temperature: 30°C, agitation: 150 rpm; adsorbent dose: 0.2 g
Temperature 25, 30, 35, 40, 45, 50 (°C)	Initial pH: 7
Agitation 50, 100, 150, 200, 300, 400 (rpm)	Contact time: 1 h; Temperature: 30°C, adsorbent dose: 0.2 g; Initial pH: 7
Adsorbent dose 0.25, 0.5, 0.75, 1.0, 1.5 (%)	Contact time: 1 h; Temperature: 30°C, agitation: 150 rpm; Initial pH: 7

The adsorption capacity was determined with the effects of contact time, initial concentration of dye solution and pH, adsorbent dosage, temperature and agitation rate. The equilibrium concentration, adsorption capacity at equilibrium were determined to fit in the adsorption isotherms. All the process factors used for adsorption experiment were referred to Table 1.

RESULTS AND DISCUSSION

Batch adsorption tests: The batch adsorption tests with the absorbent of STP biosolids showed the effective adsorption capacity by removing color from the basic dyes as a possible application of cheap and available adsorbent. Basic dyes are called cationic dyes because of the positive structures of the chromophore group. On the other hand, STP biosolids has the negative electrical charge under normal conditions[14]. Since electrical forces are the key factors which can derive the adsorption, it is probably the main reason for the good adsorption of basic dyes onto biosolids[10,15,16]. The results presented in this study showed that the maximum adsorption capacity of these basic dyes by STP biosolids was observed in the order BD-Blue>BD-Black>BD-Red.

The relationship between contact time and adsorption capacity of basic dyes by the STP biosolids was conducted through batch experiments to achieve the equilibrium as shown in Fig. 1. The results showed that the equilibrium time was reached within two hours of operation. The adsorption capacity was constant thereafter for case of all dyes observed. The basic dye BD-blue was found to be more effective for biosoprtion of STP sludge compared to the BD-Red and BD-Black. Several studies have been done to reach equilibrium at different treatment time with different types of dye using biomass[12,13,17].

The influence of the initial pH of the solution on the adsorption capacity of adsorbates by biosolids with

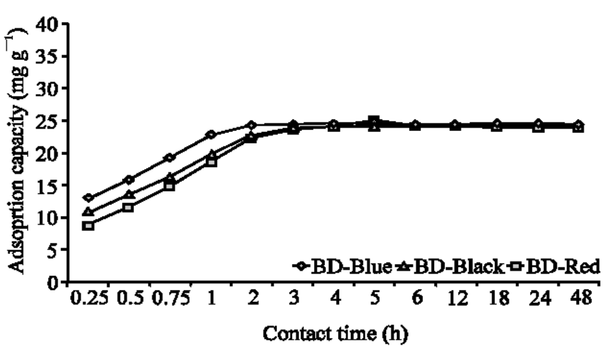

Fig 1: Adsorption capacity against contact time for adsorption of three basic dyes onto STP biosolids.

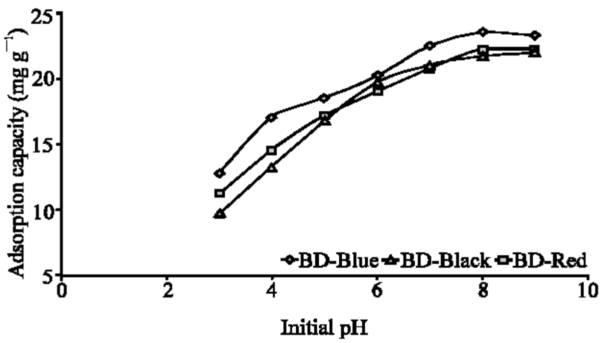

Fig 2: Effect of initial pH on the biosorption of basic dyes in aqueous solution

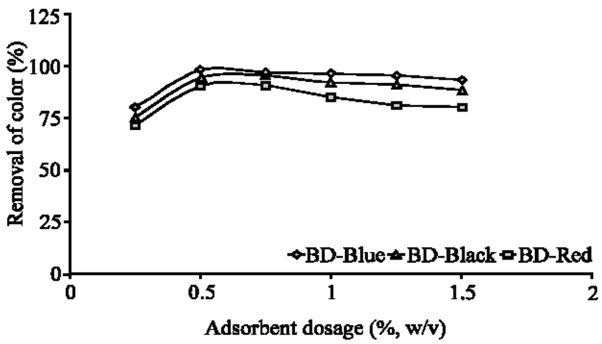

Fig 3: Removal of color from aqueous solution of basic dyes with the dosage of adsorbent

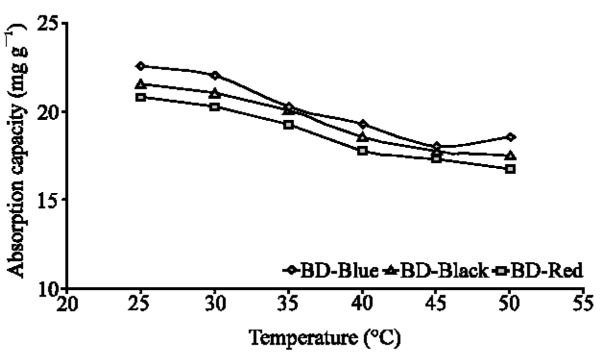

Fig 4: Effect of temperature on the adsorption capacity of various basic dyes

different conditions (Table 1) is shown in Fig. 2. The adsorption capacity was increased in increase of pH up to 8 and continued as the constant at pH 9. The higher adsorption capacity (23.5 mg g^{-1}) was recorded in aqueous solution of basic blue at pH 8. The poor adsorption of basic dyes was observed under acidic conditions (pH 3). It may be related to the presence of excess H^+ ions competing with the dye cation BD^+ (basic dye) in aqueous solution for adsorption. It is also

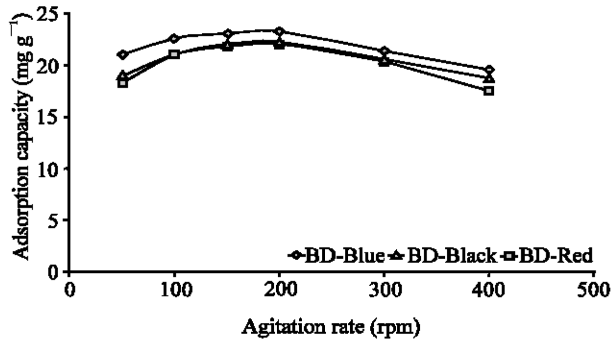

Fig 5: Variation of agitation rates for evaluating the adsorption capacity of dyes

possible that the surface properties of biosolids are depended on pH of the solution. A similar trend was observed of basic dyes by activated sludge, raw date pith as well as coir pith adsorbent[10,18,19].

In order to study the effect of adsorbent dosage on basic dyes removal as the adsorption capacity with a fixed initial concentration of dyes and pH, temperature, agitation rate, STP biomass was used as an adsorbent (Table 1). The adsorbent dosage was varied from 0.25-1.5% (w/v) to evaluate the removal rate as shown in Fig. 3. The maximum removal of 98, 90 and 94% of BD-Blue, BD-Red and BD-Black, respectively was observed with the dosage of 0.5% (w/v). The percentage removal was decreased slightly with the higher dosage (>0.5 up to 1.5% w/v) of adsorbent. It might be happened that the higher dose causes particles aggregates, overlapping and overcrowding and as a results to decrease the availability of surface area as well as decreasing the adsorption capacity[19,20]. Alam and Muyibi[21] have studied the adsorption of organic/basic dye methylene blue onto the sawdust and received the consistent as observed in the present.

The effect of temperature ranges 25-50°C on the adsorption of dyes by the STP sludge is shown in Fig. 4. The uptake of basic dyes deceased with an increase in temperature up to 50°C. The maximum dye uptake (22 mg g^{-1} for basic blue) was recorded within the temperature of 25-30°C, sharp decreased trend observed was above 30°C until to the 45°C. The adsorption capacity was decreased from 22.5 to 17.5 mg g^{-1}, 20.75 to 16.2 mg g^{-1} and 21.5 to 17.25 mg g^{-1} for the dyes of BD-Blue, BD-Red and BD-Black respectively in the solutions. The results indicated that the adsorption process is exothermic in nature[10,22]. This may be due to a tendency for the dye molecules to escape from the solid phase of biomass to the liquid phase of dyes with an increase in temperature of the solution[18,23].

A study was conducted at various agitation rates (50-400 rpm) with the constant temperature, initial dye concentration and pH to evaluate the adsorption capacity. The plot of adsorption capacity vs. agitation rates is shown in Fig. 5. A poor adsorption capacity was seen at lower agitation rate of 50 rpm as the agitation rate depends on mixing time as well as mass transfer coefficient of solid and liquid phases. The dye uptake was increased up to 200 rpm of speed and the rate was decreased at higher shaking rates (300-400 rpm). This may be due to the overcrowding and faster mixing that can be the reason of desorption of the adsorbates in the aqueous solution and hence the residual concentration of dyes were increased. Similar study has been done by Chu and Chen[10] who conducted the shaking rates 40-160 rpm with increasing uptake rates of basic dye using activated sludge.

Adsorption isotherms: Analysis of equilibrium isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes. Out of possible several isotherms equations, two have been applied for this study, the Langmuir and Freundlich isotherms.

The Freundlich isotherm has been widely adopted to characterize the adsorption capacity of organic pollutants using different adsorbents by fitting the adsorption data. The Freundlich isotherm has the general form such as:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2)$$

This equation can be modified as:

$$q_e = \frac{(C_O - C_e)}{M} = K_F C_e^{\frac{1}{n}} \quad (3)$$

where, q_e is the adsorption capacity (mg g^{-1}), C_o and C_e are the initial and equilibrium concentration (mg L^{-1}), respectively, M is the adsorbent dose (g), K_F and 1/n are the adsorption capacity and intensity of adsorption, respectively. The values of K_F and 1/n can be determined from the intercept and slope, respectively of the logarithmic plot in Eq. 3.

$$\text{In}C_e = \text{In}K_F + 1/n\,\text{In}C_e \quad (4)$$

In order to facilitate the estimation of the adsorption capacities at various conditions, the Langmuir adsorption isotherm, a typical model for monolayer adsorption was applied. The linearized Langmuir model can be written as

$$C_e/q_e = \frac{1}{K_L\ q_m} + \frac{1}{q_m} C_e \quad (5)$$

where, q_e is the amount of dye adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of dye, K_L (mg L^{-1}) and q_m (mg g^{-1}) are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption. The constants q_m and K_F can be evaluated from the intercept and slope of the linear plot of the experimental data of C_e/q_e vs. C_e.

The linearized Freundlich and Langmuir adsorption isotherms at initial dye concentration and pH 100 mg L^{-1} and 7.0, respectively, temperature 30°C, agitation rate 150 rpm were used to compare the biosorption capacity of STP biosolids for three basic dyes. The adsorption constant evaluated from the isotherms with correlation coefficients are shown in Table 2. In Table 2, very high regression coefficients (0.98-0.99) were found for all dyes. The higher regression values showed that the equilibrium data for all the basic dyes fitted well to both the Langmuir and Freundlich isotherms in the studied concentration ranges.

Based on the correlation coefficients (R^2), the equilibrium data was slightly better fitted in the Freundlich adsorption isotherm than the Langmuir equation (Table 2). The adsorption of basic dye (BD-Blue) by biosolids can be slightly better described by Freundlich equation while BD-Black by the Langmuir equation in terms of regression coefficients. Many authors have used these isotherms to evaluate the adsorption capacity by different adsorbent with different dyes[16,19,23-25].

Table 2: Freundlich and Langmuir isotherms for three different basic dyes in aqueous solutions using STP biosolids

	Freundlich[a]			Langmuir		
Basic dye	1/n	K_F	R^2	q_m (mg g^{-1})	K_L l mg^{-1}	R^2
BD-Blue	0.46	6.23	0.9976	23.2	0.042	0.9758
BD-Red	0.37	6.88	0.9767	19.4	0.055	0.9829
BD-Black	0.43	4.76	0.99	21.7	0.034	0.9851

[a]Unit of K_F was (mg g^{-1}) (mg L^{-1})^n

- The results showed that the biosorption of basic dyes onto STP biosolids was found to be effective, efficient and promising and the biosolids could be considered as a low-cost adsorbent for as well as the alternatives to commercial adsorbents for decolorization of industrial effluents (textile/dye).
- The higher biosorption capacity (22-24 mg g^{-1}) of three basic dyes was observed with the variation of process factors such as contact time of 2 h, pH of 8-9, adsorbent dosage of 0.5-0.75% w/v, temperature of 25-30°C and agitation rate of 150-200 rpm.

- The Basic Blue 3 was adsorbed well by STP biosolids compared to other two basic dyes (Basic Red 22 and Basic Black 9).
- The equilibrium data were fitted by the Freundlich and Langmuir isotherms where the data were slightly better fitted by the Freundlich isotherm for the Basic Blue 3 and Langmuir isotherm for the Basic Black 9 in terms of regression values (R^2).

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