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Adsorption of basic dyes by dried waste sludge: Kinetic, equilibrium and desorption studies

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ABSTRACT

Dried waste sludge was used as adsorbent to remove methylene blue, crystal violet and basic fuchsine using batch systems. Rate experiments were performed at various initial adsorbate concentrations, adsorbent concentration and reaction temperature. The experimental data were analyzed using several kinetic equations to determine the best-fit equation and related parameters were calculated. It was shown that the adsorption of respective dye could be best described by Ho's pseudo second order equation. The intraparticle diffusion played an important role in adsorption process. Effect of various initial adsorbent concentration and ionic strength on equilibrium was also investigated. Langmuir and Freundlich isotherms were applicable to the adsorption process and their constants were evaluated. Langmuir isotherm was found to be more suitable than Freundlich isotherm for correlation of equilibrium data. An increase in ionic strength exhibited an adverse effect on respective dye uptake. Desorption experiments showed that the loaded material could be regenerated unsatisfactorily.

Keywords: Adsorption; Desorption; Kinetics; Modeling; Waste sludge

1. Introduction

The disposal of effluents containing dyes is related to a great number of industrial operations such as textiles, tanneries, pharmaceuticals, packed food industries, pulp and paper, paint and electroplating industries. The effluents from these industries are highly colored and contain a number of other contaminants such as acids or alkalis, salts, dissolved and suspended solids and other toxic compounds [1]. In order to minimize the possible damages to human and environment arising from these effluents, various techniques have been employed for the removal of dyes from wastewaters, which principally include adsorption [2–4], photocatalytic degradation [5], electrokinetic coagulation [6], advanced chemical oxidation [7,8], ozonation [9], liquid–liquid extraction [10] and biological process [11].

Among these, adsorption process has been shown to be highly efficient for color removal from wastewater. The most commonly used adsorbent is activated carbon, which is limited due to its high cost and low selectivity [5,12]. A review of the literature has shown the possibility of using non-conventional low-cost adsorbents such as agricultural solid wastes, industrial by-products, clays, siliceous materials, zeolites, chitin and chitosan, peat, dead or living biomass, etc. for removal of dyes from aqueous solution [13].

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Sludge is by-product of the routine activities of wastewater treatment plants, the average production being estimated around 40–60 g dry matter per inhabitant per day for urban sewage plant [14]. Stringent criteria set for environmental protection will result in wastewater being treated to higher standards and hence sludge production is expected to rise in the future [15]. Conventional technologies applied to dispose of sludge mainly include landfills, forestry and land reclamation and incineration [15]. In recent years, many workers have used sludge (activated or non activated sludge) as adsorbent to remove toxic metals [16–18] and various dyes [19–22] from aqueous solution and promising results obtained.

Adsorption equilibrium and kinetics are the two important aspects for evaluation of an adsorption system as a unit operation. The aim of this study put more emphasis on investigating the effect of initial dye concentration, adsorbent concentration, reaction temperature and ionic strength on kinetics and/or equilibrium of several commonly used dyes (methylene blue, crystal violet and basic fuchsine) adsorption on to dried waste sludge from local municipal wastewater treatment plant. The suitability of several kinetic equation (i.e. modified pseudo first order equation, modified Ritchie second order equation, Ho's pseudo second order equation and Morris–Weber intraparticle diffusion model) were examined. The Langmuir and Freundlich isotherms were applied to fit the equilibrium experimental data and related constants obtained by non linear fitting analysis. Finally, desorption performance of respective dye from loaded sludge was also investigated.

2. Material and methods

2.1. Adsorbent

Waste sludge was obtained from the municipal wastewater treatment plant (anaerobic-anoxic-oxic (A2/O) unit) in Lianyungang, Jiangsu, China. Several heavy metals and metalloid concentrations in dried waste sludge were determined by ICP–MS (Cr 108, Ni 26.5, Cu 22.7, Zn 20.1, As 26.9 and Pb 46.1 mg/kg) and are below the maximum allowable concentrations (300, 200, 400, 500, 30, 500 mg/kg) in soil in China. The treatment plant investigated in this study is applied to treat the local municipal wastewater, not industrial wastewater. Hence, the contents of some toxic organic pollutants would be very small. Waste sludge was chemically activated by washing with 0.1 mol/L nitrate acid (HNO_3) four times (100 mL acid per 10 g of waste sludge) and then washed with deionized water. Chemically activated sludge was dried at 105°C to constant weight and sieved to get size fraction of 150–250 mm in diameter for subsequent adsorption experiments.

2.2. Adsorbate

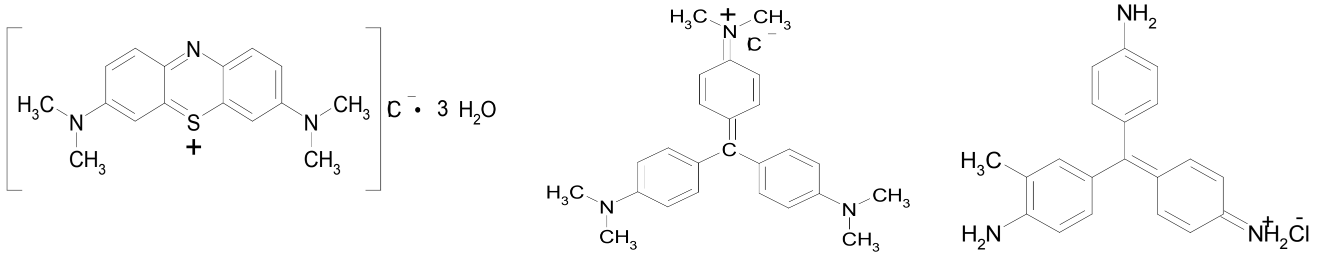
Three commonly applied basic dyes, namely methylene blue (MB), Crystal violet (CV) and basic fuchsine (BF) were selected as the representative cationic dyes. The characteristics and structural formulae of each dye are given in Table 1 and Fig. 1.

2.3. Analytical technique

The dye was made up in stock solution of concentration 1000 mg/L and was subsequently diluted to the required concentrations. Calibration curve for respective dye was prepared by recording the adsorbance values for a range of known concentrations of dye solution at the wavelength to maximum adsorbance of the dye. The value of λ_{max} (Table 1) was used in all subsequent investigations. All measurements were made on an UV/Vis spectrophotometer (UNICO-7200).

2.4. Experimental

Batch kinetic experiments were carried out with initial dye concentration of 20, 40 and 60 mg/L, respectively at adsorbent concentration of 4 g/L and 25°C. After shaking, the solution samples were withdrawn at pre-determined time intervals. At the end of each period, a known volume of the solution was removed and centrifuged for analysis. Effect of temperature was investigated at 25, 35 and 45°C, respectively with initial dye concentration of 40 mg/L and adsorbent concentration of 4 g/L. Effect of adsorbent concentration on kientics was studied at 1, 2, 3 and 4 g/L, respectively at initial dye concentration of 40 mg/L and 25°C.



MB CV BF

Fig. 1. The dye molecular structures.

Table 1
Dyes employed in the present study

Commercial name	Abbreviation	Application class	Color index	CAS number	λmax/nm	Chromopore
Methylene blue	MB	Basic blue 9	52015	7220-79-3	663	Tiazin
Crystal violet	CV	Basic violet 3	42555	603-48-5	580	Triarylmethane
Basic fuchsine	BF	Basic red 9	42500	569-61-9	540	Triarylmethane

Batch equilibrium experiments were conducted at a total sample volume of 50 ml for each adsorption run. The samples were agitated to reach equilibrium. The effect of adsorbent concentration on adsorption equilibrium was studied at 25°C by varying adsorbent concentration from 1 to 4 g/L and each used a range of initial dye concentration from 20 to 120 mg/L. Impact of ionic strength was studied at chloride sodium concentration of 0.05, 0.1 and 0.2 mol/L with initial concentration from 20 to 120 mg/L at adsorbent concentration of 4 g/L and 25°C.

Desorption tests were performed in an identical manner to the adsorption tests. But, in this case, experiments were started with dried waste sludge (0.16 g) previously loaded with known amounts of respective dye, mixed with the eluent reactant solution (H_2O, 0.1 mol/L Na_2CO_3, HCl, H_2SO_4 and HNO_3). Each experiment was performed with 200 mL of solution for 120 min.

All the batch adsorption experiments were done without adjusting the solution pH. Temperature control was provided by the water bath shaker (THZ-82, China Jiangsu Jingtan Guosheng Instrumental Factory). Each experiment was conducted in duplicate and was found reproducible (experimental error within 5%). Blanks containing no dye were also conducted at similar conditions to ensure that sorption was by adsorbent and not by the container.

2.5. Calculation

The amount of dye adsorbed at time t, q_t, was calculated from the mass balance equation

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

when time t (min) is equal to the equilibrium contact time, $C_t = C_e$, $q_t = q_e$, then the amount of dye ions adsorbed at equilibrium, q_e, was calculated using Eq. (1).

The removal efficiency (%) was computed in the following form:

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

3. Results and discussion

3.1. Kinetic study

3.1.1. Time profiles of dye adsorption

The effect of the initial concentration of respective dye used on amount adsorbed as a function of contact time is presented in Fig. 2. As shown in Fig. 2, dye uptake seemed to occur in two steps. The first step involved rapid adsorption at the beginning then being succeeded by the subsequent removal of dyestuff which continued for a relatively longer period of time until adsorption equilibrium was attained. The amount of dye adsorbed increased from 4.77 to 13.96, from 4.38 to 13.71, from 4.47 to 13.55 mg/g, when the initial concentration increased from 20 to 60 mg/L for MB, CV and BF, respectively. Initial fast rate may be ascribed to abundance of binding sites on the surface of waste sludge.

Another significant parameter to the adsorption performance is the adsorbent concentration in the bulk. The results (figure not shown) show that adsorbent concentration had a dramatic effect on both amount adsorbed and uptake rate of 20 mg/L initial dye concentration. The amount adsorbed increased from 4.74 to 18.85, from 4.38

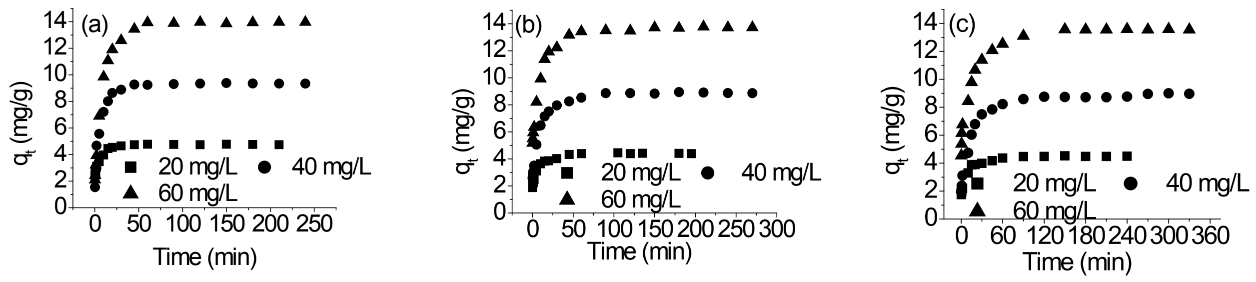


Fig. 2. Time profiles of solid-phase concentrations of various dyestuffs [(a) MB; (b) CV; (c) BF[at different initial solute concentrations (adsorbent concentration 4 g/L, temperature 25°C; mixed speed: 150 rpm; pH 6.5).

to 17.93, from 4.47 to 16.45 mg/g, when the adsorbent concentration decreased from 4 to 1 g/L for MB, CV and BF, respectively.

Reaction temperature is also an important parameter which influences the dye adsorption performance. Generally, a small effect of reaction temperature on both amount adsorbed and rate was observed (figure not shown). The equilibrium adsorption capacity was 9.33, 9.43, 9.38 mg/g for MB, 8.86, 9.02, 8.67 mg/g for CV and 8.71, 9.03 and 9.01 mg/g for BF, when the reaction temperature increased from 25 to 45°C, respectively.

In all subsequent experiments, contact time of 360 min was chosen to ensure to reach adsorption equilibrium.

3.1.2. Analysis of adsorption kinetics

In the present work, several kinetic models (i.e. modified pseudo first order equation [23], modified Ritchie second order equation [23] and Ho's pseudo second order equation [24] were used to test experimental data. These equations are given as follows:

Modified pseudo-first-order equation

$$q_t = q_e\left[1-\beta_1\exp\left(-k_1 t\right)\right] \tag{3}$$

where $\beta_1 = (1 - \theta_0)$. If the adsorbent is assumed to pre-adsorbed the impurities on the surface, the surface coverage can be assumed to a certain value ($\theta_0 \neq 0$). When $\theta_0 = 0$, then $\beta_1 = 1$, Eq. (3) becomes the Lagergren pseudo first order [25]:

$$q_t = q_e\left[1-\exp\left(-k_1 t\right)\right] \tag{4}$$

Modified Ritchie second-order equation

$$q_t = q_e\left[1-\left(\frac{1}{\beta_2 + k_2 t}\right)\right] \tag{5}$$

when the pre-adsorbed stage does not happen (i.e. $\theta_0 = 0$, then $\beta_2 = 1$), Eq. (5) becomes the Ritchie second order equation [26]:

$$q_t = q_e\left[1-\left(\frac{1}{1 + k_2 t}\right)\right] \tag{6}$$

Ho's pseudo-second order equation

$$q_t = \frac{q_e^2 k_3 t}{1+q_e k_3 t} \tag{7}$$

Eq. (7) may be rearranged for linearized data plotting as shown:

$$\frac{t}{q_t} = \frac{1}{k_3 q_e^2} + \frac{t}{q_e} \tag{8}$$

The Lagergren pseudo first order equation has been widely used in the literature for adsorption process. However, the fitting results show pseudo first order equation was not very suitable for use in the adsorption of respective dye on waste sludge. The experimental plots (data not shown) indicated that at initial stages of the adsorption process the theoretical lines (fitting lines) were higher than the data points. At the later stage, during which the theoretical lines became fairly straight horizontal lines but the experimental data points started to increase and deviate from the theoretical lines. This is in accordance with that obtained by Cheung et al. [23], who studied the Cd^{2+} adsorption onto bone char. By comparison, the modified pseudo first order equation fitted the data well (data not shown).

Ritchie second order equation and modified Ritchie second order equation were also applied to fit the experimental data points. The result shows the modified form of Ritchie second order equation was better than the Ritchie second order equation. This finding is also in agreement with that by Cheung et al. [23].

Ho's pseudo second order equation is also one of the most widely applied kinetic models. In the present study, this equation was applied to fit the experimental data and the corresponding parameters calculated using non linear analysis as well (data not shown). The parameter of k_3 declined with increasing initial solution concentration for various dyes and increased with increasing adsorbent concentration only for CV and BF dyes. The effect of reaction temperature on k_3 variation was irregular and only the k_3 for the adsorption of BF increased with increasing reaction temperature.

The comparisons between the calculated using these kinetic equations mentioned above and experimental results for MB adsorption on sludge were conducted (data not shown) and the results show that at the initial stage, these three kinetic equations fitted the experimental data points equally well; but the modified pseudo first order equation slightly underestimated and the modified pseudo second order equation slightly overestimated at the later stage.

3.1.3. Mechanistic analysis of adsorption kinetics

The Lagergren pseudo first order equation and Ho's pseudo second order equation basically include all steps of adsorption such as external film diffusion, adsorption, and internal particle diffusion, so they are pseudo-models and cannot identify adsorption mechanisms [27–29]. Accordingly, the intraparticle diffusion model was further tested.

Intraparticle diffusion model used here refers to the empirical equation proposed by Weber and Morris [30] and is simply written as

$$q_t = k_4 t^{0.5} \tag{9}$$

In order to examine the applicability of intraparticle diffusion in fitting kinetic data, the amount adsorbed, q_t vs. the square root of time, $t^{0.5}$ for MB adsorption on waste sludge at different conditions are plotted (data not shown). The initial linear relationship between q_t and $t^{0.5}$ confirmed the contribution of the intraparticle diffusion mechanism in the adsorption process. However, the intercept did not pass through the origin, indicating that the intraparticle diffusion was not the only rate-limiting step [28]. These findings are in agreement with those obtained by other workers [27,31].

For intraparticle diffusion controlling systems, the product of k_4 times adsorbent concentration (m_s) should vary linearly with adsorbent concentration [32]. Fig. 3 represents the plot of $k_4 \cdot m_s$ against m_s, which indicated adsorption onto waste sludge was intraparticle diffusion controlled process.

Similarly, when intraparticle diffusion controls the kinetics of an adsorption process, the rate constant k_4 varies with some power of the initial adsorbate concentration C_0 [19]. The relationship between rate constant k_4 and initial adsorbate concentration C_0 is expressed by these empirical equations for MB, CV and BF, respectively

$$k_4 = 0.0122C_0^{1.3067} \qquad r^2 = 0.9701 \tag{10}$$

$$k_4 = 0.0301C_0^{0.9955} \qquad r^2 = 1.0 \tag{11}$$

$$k_4 = 0.0968C_0^{0.6117} \qquad r^2 = 0.9128 \tag{12}$$

Inspection of the exponential value of initial dye concentration C_0 also suggests that intraparticle diffusion was the limiting-step in the respective dye adsorption process.

3.1.4. *Effect of temperature on rate constant*

The effect of reaction temperature on respective dye adsorption was examined in greater details by applying the Eyring equation on the rate constant data. Azizian [33] used a theoretical approach to analyze the pseudo second order model and found that the pseudo second order rate constant was not an intrinsic adsorption rate constant but a complex function of the initial concentration of solution. Accordingly, the pseudo second order rate constant, k_3, was not applied to calculate the corresponding thermodynamic parameters.

The activation enthalpy ($\Delta H_\#^o$) and activation entropy ($\Delta S_\#^o$) for the respective dye adsorption process were obtained using the Eyring equation [34]:

$$k = \frac{RT}{Nh} e^{(\Delta S_\#^0 / R)} e^{(-\Delta H_\#^0 / RT)} \tag{13}$$

The linearized form of Eq. (13) is

$$\ln \frac{k}{T} = \ln \frac{R}{Nh} + \frac{\Delta S_\#^0}{R} - \frac{\Delta H_\#^0}{RT} \tag{14}$$

Therefore, the plot of ln [k/T] vs. $1/T$ yields a straight line, from which the $\Delta H_\#^o$ and $\Delta S_\#^o$ can be obtained based on the slope and intercept, respectively.

The activation free energy, $\Delta G_\#^o$, kJ/mol was obtained using the following relation:

$$\Delta G_\#^0 = \Delta H_\#^0 - T\Delta S_3^0 \tag{15}$$

Plotting the ln [k/T] against $1/T$ yielded a linear relationship for MB and BF adsorption onto waste sludge (not shown) and the calculated values of $\Delta G_\#^o$, $\Delta H_\#^o$, and $\Delta S_\#^o$ are summarized in Table 2. The fact that $\Delta H_\#^o$ values are relatively low was also an indication of a diffusion controlled process [35,36]. The negative values of $\Delta S_\#^o$ indicated that decreased randomness at the solid/solution interface during the MB and BF adsorption on waste sludge. The positive $\Delta G_\#^o$ values at 25, 35 and 45°C suggested the non-spontaneous nature of adsorption for MB and BF. A convex Eyring plot for CV adsorption means that $\Delta H_\#^o$ decreased with increasing temperature.

3.2. *Equilibrium study*

3.2.1. *Effect of initial solute concentration and adsorbent concentration*

The effects of initial dye concentration on various dye uptakes were investigated. The result shows that the higher the initial concentration of the dye, the larger the amount adsorbed. When the initial dye concentration was increased from 20 to 120 mg/L, the loading capacity (amount adsorbed per gram of adsorbent) increased from 13.8 to 59.1 mg/g of MB, from 15.3 to 64.5 mg/g for CV, and from 12.8 to 65.7 mg/g for BF, respectively, at the adsorbent concentration of 1 g/L. The increases in amount adsorbed with the increases of dye initial concentration

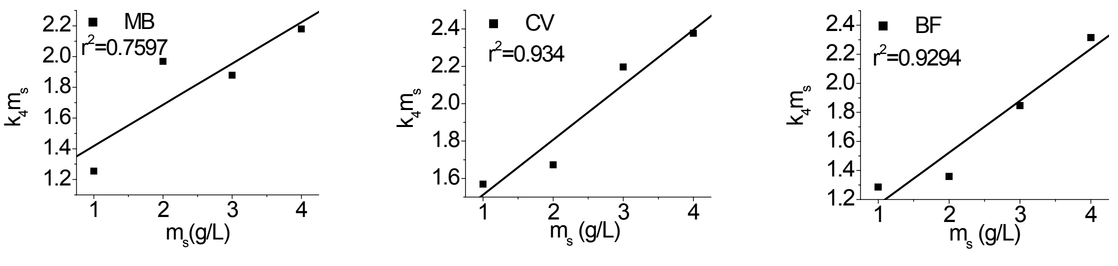


Fig. 3. Plots of $k_4 \cdot m_s$ vs. m_s.

Table 2
Thermodynamic parameters of various dyes adsorption onto waste sludge (The data for CV were not obtained because the plot of ln [k/T] vs. $1/T$ did not yield a straight line.)

Dye	Temperature (°C)	k_1			k_2		
		$\Delta G^{o}_{\#}$	$\Delta H^{o}_{\#}$	$\Delta S^{o}_{\#}$	$\Delta G^{o}_{\#}$	$\Delta H^{o}_{\#}$	$\Delta S^{o}_{\#}$
MB	25	87.9	6.4	–273.8	86.0	11.9	–248.5
	35	90.7			88.5		
	45	93.4			91.0		
BF	25	90.1	41.7	–162.5	88.4	54.65	–113.5
	35	91.7			89.6		
	45	93.3			90.7		

may be attributed to the higher collision probability between adsorbate and adsorbent [37].

The adsorbent concentration also appreciably affected the equilibrium uptake (data not shown). At 20 mg/L of initial dye concentration, with the variation of adsorbent concentration from 1 to 4 g/L the uptake capacity decreased from 13.8 to 4.6 mg/g of MB, 15.3 to 4.2 mg/g for CV and from 12.8 to 4.1 mg/g for BF, respectively. Higher removal efficiency was observed at higher adsorbent concentration for the given initial dye concentration.

3.2.2. Adsorption isotherm

In the present study, two widely used isotherms (i.e., Langmuir [38] and Freundlich equations [39]) have been applied to test the isothermal data. These two equations are written as, respectively

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \tag{16}$$

$$q_e = k_f C_e^{1/n} \tag{17}$$

The isotherm constants evaluated from the isotherms using non-linear fitting analysis with the correlation coefficients (r^2) are given in Table 3.

The value of $q_{\max}$ (maximum adsorption capacity) appeared to be significantly larger for BF-sludge system in comparison with the uptakes of MB and CV on waste sludge. The difference in $q_{\max}$ of respective dye is ascribed to be affected by a combination of factors including dye molecular structure, molecular weight and ionic radius [1,19]. The large value of b suggested strong binding of CV to the waste sludge.

The constant, k_f, derived from the Freundlich equation is an indicator of adsorption capacity of a given adsorbent while the exponent, n, is related to the affinity or binding strength [40]. The constants k_f and n values were listed in Table 3. The value of n was greater than unity, indicating a favorable adsorption process for respective dye studied.

Examination of the data in Table 3 showed the Langmuir equation was an appropriate description of the data for respective dye adsorption over the concentration ranges studied. The validity of the Langmuir equation suggested the adsorption process for various dyes was monolayer and adsorption of each dye molecule had equal activation energy.

Table 4 shows a comparison between the results of this work and others found in the literature. Few data on BF adsorption from aqueous solution were available for comparison. The qmax value of MB found in this work was higher than those of some reported low-cost adsorbents such as Streptomyces rimosus, lignite coal, wheat bran and clay. In contrast, the qmax of CV found in this study was comparable with values found in the literature. These indicate that the waste sludge investigated could be used to remove these three basic dyes from aqueous solution.

The effect of isotherm shape can be used to predict

Table 3
Isotherm constants for various dyes uptake on waste sludge (adsorbent concentration 1 g/L; temperature 25°C, mixed speed: 150 rpm; pH 6.5)

	Langmuir			Freundlich		
	$q_{\max}$	b	r^2	k_f	n	r^2
MB	86.91	0.0372	0.9940	7.53	1.941	0.9733
CV	89.74	0.0521	0.9957	10.37	2.108	0.9717
BF	127.07	0.0207	0.9913	5.03	1.524	0.9779

Table 4
Comparison between the results of this work and others found in the literature

Adsorbents	$q_{\max}$ (mg/g)	Reference
MB		
Activated carbon	296.3	[41]
Activated sludge biomass	256.41	[42]
Sewage sludge	114.94	[15]
Waste sludge	86.91	This work
Raw date pits	80.3	[44]
Rice bran	54.99	[45]
Streptomyces rimosus	34.3	[46]
Lignite coal	32	[47]
Fe(III)/Cr(III) hydroxide	22.8	[48]
Wheat bran	16.62	[45]
Clay (Turkey)	6.3	[49]
CV		
Waste sludge	89.74	This work
Wheat bran	72.76	[50]
Laminaria japonica	59.73	[50]
Rice bran	44.75	[50]
BF		
Waste sludge	127.07	This work

whether adsorption system is "favorable" or "unfavorable" both in fixed-bed system as well as in batch process [51]. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, K_L, which is defined as [52]

$$K_L = \frac{1}{1 + bC_0} \tag{18}$$

The value of K_L indicates the shape of the isotherm as follows:

K_L value	Type of isotherm
$K_L > 1$	Unfavorable
$K_L = 1$	Linear
$0 < K_L < 1$	Favorable
$K_L = 0$	Irreversible

In the present investigation, the values of separation factor, K_L, are in between 0 and 1, indicating that the adsorption process was favorable and the adsorbent employed exhibited an optimum potential for respective dye. According to this classification, system favor ability tends to be in the order of CV > MB > BF.

3.2.3. Effect of ionic strength

Dye-laden wastewaters released from different industries contain various types of salts and the salt concentration is up to 15–20% [53]. The presence of these salts leads to high ionic strength, which may significantly affect the performance of the adsorption process [1,53]. Fig. 4 shows clearly that the variation of sodium chloride concentration exhibited a major effect on the extent of respective basic dyes adsorption at different initial concentration. The amount of respective dye adsorbed decreased under the condition that the concentration of chloride sodium increased at each given initial dye concentration. This finding is in agreement with those obtained by Maurya et al. [1]. The decrease in amount adsorbed with increased ionic strength may be attributed to the following reasons: the Na^+ ions competed against the dye ions for binding sites of the waste sludge and the Cl^- ions shielded dye ions and the charged binding sites from each other [54].

3.3. Desorption study

A preliminary evaluation of the desorbing agents was carried out under batch experimental condition and desorption efficiencies were compared in Fig. 5. The use of deionized water (control) and 0.1 mol/L Na_2CO_3 showed insignificant desorption (less than 5%) for various dyes. By contrast, mineral acids (0.1 mol/L HCl, H_2SO_4 and HNO_3) resulted in relatively high recovery efficiencies of about 25.8, 17.3 and 14.2% for MB, 30.8, 18.6 and 24.4%

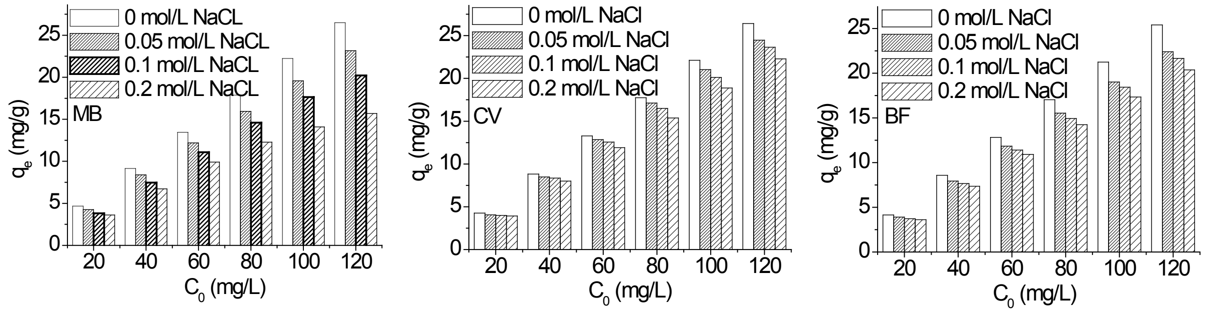


Fig. 4. Plots of q_e vs. C_0 at different supporting electrolyte concentrations (25°C; adsorbent concentration of 4 g/L; mixed speed: 150 rpm; pH 6.5).

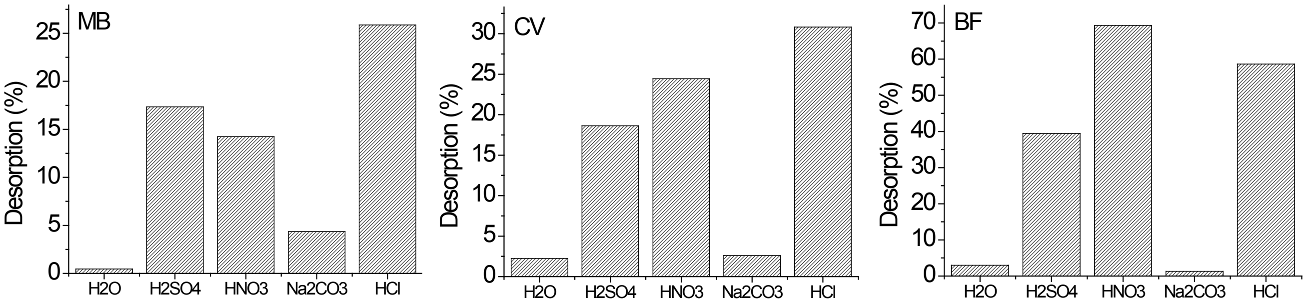


Fig. 5. Desorption efficiencies of various dyes using different desorbing agents.

for CV, and 58.6, 39.4 and 69.3% for BF. The low regenerability of loaded sludge is likely an indication of strong affinity between adsorbate and adsorbent.

4. Conclusions

The adsorption kinetics and isotherm of three commonly used basic dyes were investigated at various initial adsorbate concentration, adsorbent concentration, reaction temperature or ionic strength in batch experimental system. The following results were obtained:

1. The adsorption rate of dye onto waste sludge was particularly sensitive to initial adsorbate concentration and adsorbent concentration but almost insensitive to reaction temperature.
2. The adsorption process of respective dye on waste sludge could be well described by Ho's pseudo second order equation. The intraparticle diffusion played an important role in respective dye adsorption process.
3. The thermodynamic parameters revealed that the MB and BF adsorption process was endothermic and non-spontaneous in nature.
4. The best interpretation for the equilibrium data was given by Langmuir isotherm.
5. An increase of dye uptake by waste sludge was observed with higher adsorbent concentration and lower ionic strength.
6. Desorption experiments showed that the loaded material could be regenerated unsatisfactorily.

Symbols

b — Freundlich constant, L/mg
C_0 — Initial concentration of solute in aqueous phase, mg/L
C_e — Concentration of solute in aqueous phase at equilibrium, mg/L
$\Delta G^{o}_{\#}$ — Activation free energy change, kJ/mol
$\Delta H^{o}_{\#}$ — Activation enthalpy change, kJ/mol
h — Planck constant, 6.626×10^{-34} J s
k_1 — Rate constant of modified pseudo first order equation, 1/min
k_2 — Rate constant of modified Ritchie second order equation, 1/min
k_3 — Rate constant of Ho's pseudo second order equation, g/(mg min)
k_4 — Rate constant of intraparticle diffusion equation, mg/(g min$^{0.5}$)
k_f — Freundlich constant, (mg/g)/ (mg/L)$^{1/n}$
K_L — Separation factor, dimensionless
m — Mass of sorbent, g
m_s — Adsorbent concentration, g/L
N — Avogadro constant, 6.022×10^{23} 1/mol
n — Freundlich constant
q_e — Sorption capacity at equilibrium, mg/g
$q_{\max}$ — Freundlich constant, mg/g
q_t — Sorption capacity at time t, mg/g
R — Gas constant, 8.314 J/mol K
r^2 — Correlation coefficient, dimensionless
$\Delta S^{o}_{\#}$ — Activation entropy change, J/mol K
T — Absolute temperature, K
t — Time, min
V — Volume of solution, L

Greek

β_1 — Constant of modified pseudo first order equation, ($\beta_1 = 1 - \theta_0$)
β_2 — Constant of modified Ritchie second order equation, ($\beta_2 = 1/(1 - \theta_0)$)
$\lambda_{\max}$ — Maximum absorption wavelength
θ — Surface coverage at time t, ($\theta = q_t/q_e$)
θ_0 — Surface coverage at pre-adsorbed stage, ($\theta_0 = q_0/q_e$)

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