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Batch sorption of iron complex dye, naphthol green B, from wastewater on charcoal, kaolinite, and tafla

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ABSTRACT

The effective removal of dyes from industrial wastewater is one of the most important issues for many industrialized countries. Dyes are commonly used in many industries to color the final products, in chemical and radiochemical laboratories for analytical purposes. The feasibility of using commercial charcoal and two important and common clay minerals, kaolinite, and tafla, as low-cost adsorbents for removal of iron complex dye has been investigated by batch technique. The effects of solution pH, equilibration time, initial dye concentration, and temperature have been studied and discussed. The obtained results have indicated that the sorption is rapid and acidic pH is favorable for the sorption of naphthol green B. The results of adsorption experiments indicate that the monolayer capacity of naphthol green B dye at equilibrium is 232.56, 25.80, and 23.86 mg g^{-1} for charcoal, kaolinite, and tafla, respectively. The amount of dye removed increased with increasing temperature, which indicates the endothermic nature of the sorption process. The parameters can be used for designing a plant for treatment of wastewater economically.

Keywords: Iron complex dye; Naphthol green B; Sorption; Charcoal; Kaolinite; Tafla

1. Introduction

The increased level of environmental pollution as a successive of industrial development is posing a very dangerous problem to the global environment. The main sources of water pollution are from agricultural, industrial and domestic activities, and other environmental changes. The surface and ground water in many places all over the world is contaminated with hazardous materials and does not fit drinking purposes. By 2020, the world population is supposed to reach up to about 7.9 billion and the world may experience the great scarcity of fresh water [1,2]. Therefore, the removal of hazardous materials, such as dyes and heavy metals, from industrial effluents is of great environmental concern [1].

Dyes are used in large amounts in laboratories and many industries, including leather, textile, paper, cosmetics, plastic, pharmaceuticals, and food, to color their products. Dyeing in the textile industry uses large amounts of water and generates high volumes of colored wastewaters. In this industry, a fair estimation of dyes losses to the environment effluents are about 1–2% during their production and 1–10% during their utilization [3,4]. The remaining dyes, even at low amounts, in the wastewater are common water

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pollutants. Most of the commercially used dyes are either toxic and mutagenic and carcinogenic due to the presence of toxic ions in their structure. In addition, their presence in water is highly visible and undesirable, and may negatively affect photosynthetic activity in aquatic life [4–7].

The dye-containing colored water is hardly of any use, but if the colored solutions are bleached to give colorless water, it may be used for washing, cooling, irrigation, and cleaning purposes [8]. Dyes, which are chemically and photolytically stable, can be removed from wastewater by sorption, flotation, coagulation, oxidation, electrodialysis, cloud-point extraction, etc. [5,9].

The treatment of wastewaters by sorption process is an attractive choice, especially if the sorbent used is low cost, readily available, and does not require any additional pretreatment step before its use [4]. It is now established that sorption technique is one of the most powerful tools for the removal of pollutants from water and the technique has several advantages over other physicochemical methods. The abilities of the sorption process to remove and recover the larger organic compounds, without their decomposition, have also popularized it over other modern electrochemical and photochemical methods [10]. The widely used sorbents to remove dyes in wastewater employs activated carbon; however, its use is restricted due to its high cost and the difficulty to reuse [11].

Recently, much attention has been focused on developing other low-cost and commercially available alternatives to carbon adsorbent, such as fly ash, agricultural wastes, metal hydroxides sludge, and wood wastes. Natural clay materials have received wide attention due to their low cost and structural properties, such as montmorillonite, kaolinite, and activated clay [4,10,11].

Metal complex dyes, as an important class of dyes, have been extensively used in textile dyeing, color photography, cosmetic, paper printing, drug, food, and other industries. It is estimated that metal complex dyes account for 30% of dyes in wool dyeing industry and 40% in polyamide dyeing industry [12]. Metal complex dyes are the strong complexes of one metal atom and one or two dye molecules, and can be found in textile finishing wastewater when using acid, direct, and reactive dyes, as well as pigments [13]. Environmental concerns arise from the carcinogenic properties of these metals and from amines formed by reductive cleavage of azo groups of organics. Therefore, the removal of metal complex dyes has been targeted as one of the most important issues in textile wastewater treatment [12,13]. However, only a limited number of studies on the removal of metal complex dyes have been found in the literature, especially naphthol green B [4,14].

Naphthol green B (1-nitroso-2-naphthol-6-sodium sulfonate ferric salt), is an important dye. The anion form acts as acid dye and possesses redox properties. This type of dye is able to undergo electro-polymerization from aqueous solution, producing stable active redox layers. Therefore, naphthol green B can be used as a mediator for electrocatalysis of dopamine and uric acid because of its high electron transfer efficiency and low cost [15]. Naphthol green B is used also as analytical reagent in many spectrophotometeric determination methods [16].

Clays are fine-grained natural materials; kaolinite and tafla clays are found as a common constituent of soils and sediments and rocks.

The trials towards the treatment of naphthol green B from wastewater is still limited. In this paper, we report our investigation in utilization of commercial charcoal, kaolinite, and tafla as adsorbents for removal of iron complex dye (naphthol green B) as these materials are very abundant and inexpensive.

2. Experimental

2.1. Materials and instruments

The dye used in this study, naphthol green B dye, was supplied from Aldrich. The naphthol green B aqueous solution used in this study was a synthetic wastewater. A stock solution of 1,000 mg l^{-1} of naphthol green B was prepared by dissolving 1 g of dye in 1,000 ml of double distilled water and used for further studies by diluting at the required concentrations. The structure of dye naphthol green B is presented in Fig. 1 and the properties of the dye are presented in Table 1.

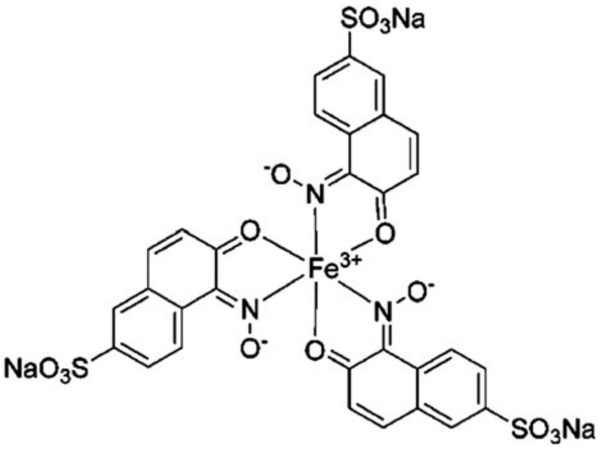

Fig. 1. Structure formula of naphthol green B dye.

Table 1
Characteristics of naphthol green B dye

Parameter	Value
Chemical name	Naphthol green B
Type	Anionic (Azo-metal complex)
Molecular formula	$C_{30}H_{15}FeN_3Na_3O_{15}S_3$
Molecular weight	878.46 g mol
λ_{max}	714 nm
Color index number	10,022
Appearance (color)	Solid dark green powder
Solubility	Soluble in water (160 mg ml^{-1}), ethanol (0.9 mg ml^{-1}), ethylene (9 mg ml^{-1})

All the reagents used in this study are of analytical reagent grade. The initial pH was adjusted to the required value using NaOH or HCl solutions after addition of the adsorbent. The kaolinite and tafla used for the adsorption tests were collected from Abu Zeneima (Sinai) and Katameyya (Cairo) region in Egypt; the samples were sieved and those with a mean size of 200 and 53 μm were used in the experiments. The samples were dried for 1 h in an oven maintained at 125˚C, allowed to cool to room temperature, and then were directly used as adsorbent without any chemical and physical treatment as this would be the most economical commercial product. Commercially available charcoal was supplied from El Nasr Pharmaceutical Chemicals Company (Adwic), Egypt.

Most of the samples used in this work were weighed using an analytical balance of Precisa 205A type having maximum sensitivity of 10^{-3} g and an accuracy of ±0.01 mg. The pH of the different solutions was measured using a digital pH-meter of the type CG 820, Germany, within an error of ±0.01. For the equilibration experiments, the aqueous and adsorbents were mixed together using a thermostated mechanical shaker of the type Julabo SW-20C, Germany, controlled within ±1˚C and with stirring range from 20 to 2,000 rpm. The absorption spectra of the solutions were measured using a "Shimadzu" UV–visible spectrophotometer Model UV-160A, with a fixed slit width (2 nm), Japan.

2.2. Batch adsorption experiments

The adsorption test on the charcoal, kaolinite, and tafla (adsorbents) was performed in order to determine the time needed to reach equilibrium and the pattern of the kinetics. For this purpose, samples of 0.01 g of charcoal and 0.1 g of kaolinite and tafla were transferred into glass bottles containing 12.5 ml of 100 mg l^{-1} naphthol green B dye solution. The bottles were placed at 27 ± 2˚C using a temperature-controlled shaker for 1 h. The samples were taken from the shaker at predetermined time intervals. The residual concentration of naphthol green B at any time, t, was determined from the absorbency measured with a UV–vis spectrophotometer at 714 nm wavelength, at which the maximum absorbance occurred.

2.3. Data analysis

The percentage removal, $R\%$, of the naphthol green B dye at equilibrium and the amount of naphthol green B transferred onto the surface of the adsorbent at time t, q_t (mg g^{-1}) and at equilibrium q_e (mg g^{-1}), were calculated using the following relationships [4]:

$$R\% = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

$$q_t = (C_0 - C_t)\frac{V}{m} \tag{2}$$

$$q_e = (C_0 - C_e)\frac{V}{m} \tag{3}$$

where q_t shows the amount of naphthol green B adsorbed on the adsorbent at time t. C_0, C_t, and C_e represent the naphthol green B concentrations in the solution (mg l^{-1}) at initial, time t and equilibrium, respectively. V is the volume of solution (l) and m is the mass of adsorbent (g).

3. Results and discussion

In this paper, an attempt has been made to suggest certain low-cost materials as effective adsorbents of iron complex dye, naphthol green B (NGB). The uptake was accomplished under the optimum conditions of temperature, concentration, pH, contact time, and quantity of adsorbent as these parameters are some of the main factors influencing the uptake of the solute at the solid–solution interface.

3.1. Effect of initial pH

The pH of the adsorption system is one of the most important factors controlling the adsorption of the adsorbate onto the adsorbent, since the surface charge of a solid phase (adsorbent) could be modified by changing the pH of the solution and the ionization/dissociation of the adsorbate molecule [10,11]. Batch studies have been performed for the adsorption of NGB dye onto charcoal, kaolinite, and tafla by varying the pH from 2.5 to 10.5 at a fixed initial dye concentration of 100 mg l^{-1}, 0.01 g of charcoal, and 0.1 g of kaolinite and tafla. From the study, the removal of the NGB dye is highly pH dependent, which can be shown in Fig. 2.

It is evident that the NGB sorption is higher at lower pH and as the pH of the solution increases, it decreases sharply. Similar pH trends were reported by other researchers [4,17]. Higher removal obtained at acidic range may be due to the electrostatic attractions between negatively charged functional groups located on the NGB dye and positively charged adsorbents surface. Hydrogen ion also acts as a bridging ligand between the adsorbent wall and the dye molecule [18]. However, two possible mechanisms of adsorptive removal of NGB dye on three adsorbents may be considered: (a) electrostatic interaction between the three adsorbents and NGB dye and (b) the chemical reaction between the NGB dye and the adsorbents.

Low pH value (acidic range) leads to an increase in hydrogen ion concentration in the adsorption system and the surface of the three adsorbents acquires positive charge by absorbing hydrogen ions, thereby increasing the adsorption of NGB dye. As the adsorbent surfaces are positively charged in acidic range, a significantly strong electrostatic attraction appears between the adsorbents surfaces and NGB anions leading to maximum adsorption of NGB dye. On the other hand, the increase in the pH value (basic condition) led to the increase in the number of negatively charged sites in which the number of positively charged sites decreases. A negatively charged surface site on the three adsorbents is not favoring for adsorption of NGB dye anions due to the electrostatic repulsion [4,11,18].

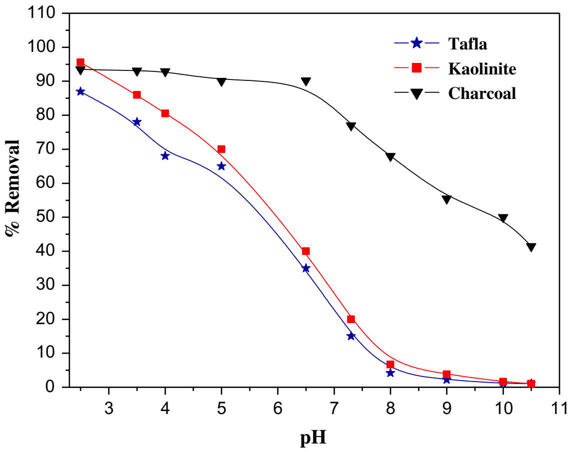

Fig. 2. Effect of pH on adsorption of NGB dye onto charcoal, kaolinite, and tafla.

It is reported that [19] adsorption of anions on surface hydroxyl groups (especially in kaolinite and tafla case) is coupled with a release of OH^{-} ions, and the main mechanism is ligand exchange. It can be assumed that OH^{-} ions were replaced by SO^{-3} ions because the sulfonic group is a strongly acidic cation exchanger [20], resulting in the charge balance of the precipitate to be settled, as illustrated in the following equations:

$$M - (OH)_n \rightleftharpoons M - (OH)^{+}_{n-1(aq)} + OH^{-}_{aq} \tag{4}$$

$$Dye - SO_3Na \rightleftharpoons Dye\text{ - }SO^{-}_{3(aq)} + Na^{+}_{(aq)} \tag{5}$$

$$M - (OH)^{+}_{n-1(aq)} + Dye - SO^{-}_{3(aq)} \rightleftharpoons M - (OH)_{n-1}O_3S - Dye_{(s)} \tag{6}$$

where n = 2 or 3. Generally, a positive charge develops on the surface of oxides of adsorbents in an acid medium, resulting in a higher adsorption of NGB dye than in a basic solution, as reported [4]. Many sulfonated dyes can be made insoluble by precipitating them as the salts of heavy metals or as dye metal complexes with soluble salts of heavy metal ions [4,21]. The removal of dye at pH 2.5–7 may result from the complexation between the dye and metal ions, yielding a precipitate. NGB dye has a higher number of negative sites available for adsorption or exchange. Appreciable amount of adsorption in this pH range suggests a strong involvement of physical forces, such as hydrogen bonding, van der Waals force, etc., in the adsorption process.

3.2. Effect of contact time and initial concentration on the NGB removal

The equilibrium time is one of the most important parameters in the design of economical wastewater treatment application [17]. Sorption experiments were carried out on charcoal, kaolinite, and tafla with adsorbent dosage of 0.01 g charcoal at pH 6 and 0.1 g from kaolinite and tafla at pH 4. Figs. 3–5 illustrate the sorption of NGB dye on charcoal, kaolinite, and tafla from aqueous solution as a function of contact time and initial concentration. It is clear that the sorption of NGB dye on the three adsorbents increases with the contact time. The maximum sorption of NGB on the three sorbents was achieved almost within 60 min with charcoal and about 40 min with kaolinite and tafla, and the sorption remained nearly constant with further increase in contact time. Short sorption equilibrium time favors the application of the sorption process. The sorption equilibrium time required for NGB sorption by the three selected adsorbents was considered to be relatively short.

In addition, for the NGB dye sorption on three adsorbents, a rapid removal of NGB was observed in the initial stage of contact time, and the NGB removal rate gradually decreased with lapse of time until the curves appeared to level off, Figs. 3–5.

The effect of NGB dye concentration in the range from 100 to 200 mg l^{-1} on the sorption of NGB dye was also investigated, Figs. 3–5. The sorption capacity of three adsorbents increased with increasing the NGB concentration. This indicates that the sorption is highly dependent on the initial concentration of the NGB dye. The initial concentration provides an important driving force to overcome all mass transfer resistances of the NGB between the aqueous and solid phases. Hence, a higher initial concentration of the dye will enhance the sorption process [17].

3.3. Sorption kinetic study

Sorption kinetics shows the large dependence on the physical and/or chemical characteristics of the sorbent material, and sorbate species which also influence the sorption mechanism [11]. The contact time experimental results can be used to study the rate-limiting step in the removal process. The overall sorption process may be controlled either by one or more steps like film or external diffusion, pore diffusion, surface diffusion, and adsorption on the pore surface or a combination of more than one step.

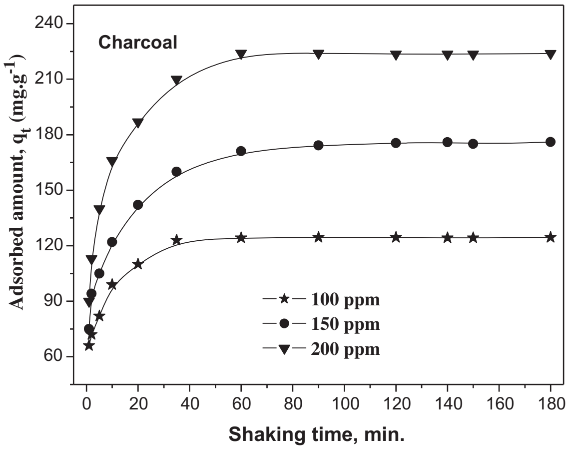

Fig. 3. Effect of contact time and initial concentration on the NGB uptake using charcoal.

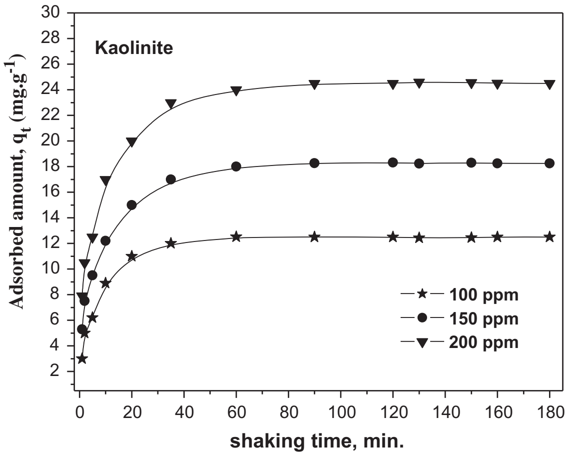

Fig. 4. Effect of contact time and initial concentration on the NGB uptake using kaolinite.

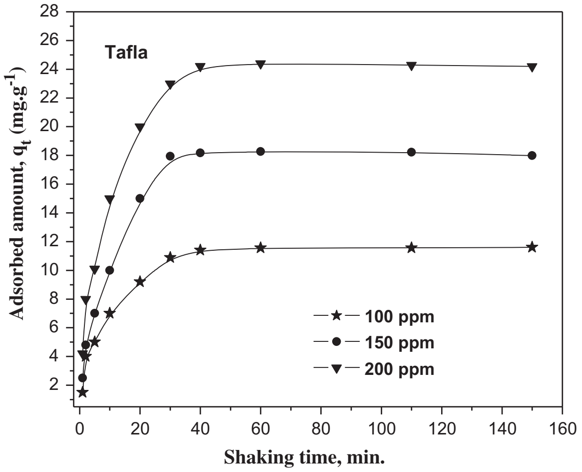

Fig. 5. Effect of contact time and initial concentration on the NGB uptake using tafla.

Sorption kinetics is usually modeled by the pseudo-first-order equation of Lagergren and the pseudo-second-order rate model. Thus, pseudo-first- and pseudo-second-order kinetic models [4,11,22–24] were studied for sorption of NGB dye onto charcoal, kaolinite and tafla. The conformity between experimental values and the model-predicted values is expressed by the correlation coefficients (R^2, values close or equal to 1; the relatively higher value is the more applicable model).

The first model used to describe the kinetics of the sorption of NGB dye onto charcoal, kaolinite, and tafla is the pseudo-first-order model, which the earliest known equation is describing the adsorption rate based on the adsorption capacity. Pseudo-first-order model is presented by the Lagergren equation as the following [11,22–24]:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_1(q_e - q_t) \tag{7}$$

Integrating this equation for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$, it leads to the following equation:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{8}$$

where k_1 is the apparent pseudo-first-order rate constant (in min^{-1}), q_t is the extent of sorption at time t (in mg/g), and q_e is the extent of sorption at equilibrium (in mg/g). Pseudo-first-order kinetic model is used for estimating k_1 alone, which is considered as mass transfer coefficient in the design calculations [23,24].

By plotting log ($q_e - q_t$) vs. t, straight lines were obtained; from the slope and the intercept, one can determine the values of pseudo-first-order rate constant, k_1, and the calculated sorbed amounts at equilibrium, q_e, calc. as illustrated in Table 2. Despite the correlation coefficients for the plot of pseudo-first-order kinetic model obtained for the NGB dye are quite high, the calculated q_e values do not give reasonable values, and are not close to the experimental values; thus, the sorption of NGB dye onto charcoal, kaolinite, and tafla do not fit Lagergren equation, Fig. 6.

The second model used to describe the kinetics of the sorption of NGB dye onto the charcoal, kaolinite, and tafla is the pseudo-second-order model, which is presented by the following equation [23]:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2(q_e - q_t)^2 \tag{9}$$

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of the above equation becomes:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{10}$$

The values of the pseudo-second-order rate constant, k_2, in g mg^{-1} min^{-1}, and the amount adsorbed at equilibrium, q_e, can be determined from the slope and the intercept of the plots of t/q vs. t, respectively. Fig. 7 gives straight lines from which the values of k_2 and q_e are determined. Table 2 illustrates that the calculated q_e values are closer to the experimental data than the calculated values of the pseudo-first-order model, and the correlation coefficients are very high for the pseudo-second-order kinetic model. This suggests that the sorption of NGB dye on the three adsorbents may be best described by the pseudo-second-order kinetic model, thus reinforcing the applicability of this model. This conclusion indicates that the rate-limiting step is chemical sorption.

Table 2
The calculated parameters of the pseudo-first-order and pseudo-second-order kinetic models of NGB dye for adsorption onto charcoal, kaolinite, and tafla

		Pseudo-first-order parameter			Pseudo-second-order parameter			
Adsorbent	Conc. (mg l^{-1})	k_1 (min^{-1})	q_e, calc. (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e, calc. (mg g^{-1})	R^2	q_e exp. (mg g^{-1})
Charcoal	100	0.099	70.28	0.987	0.005	126.0	0.999	122.1
	150	0.046	88.53	0.994	0.002	179.5	0.999	176.0
	200	0.041	85.68	0.983	0.002	227.8	0.999	224.0
Kaolinite	100	0.086	9.256	0.994	0.043	12.644	0.999	12.40
	150	0.051	9.555	0.967	0.016	18.685	0.999	18.31
	200	0.042	11.320	0.955	0.012	25.107	0.999	24.60
Tafla	100	0.092	10.953	0.991	0.0153	12.142	0.999	12.39
	150	0.130	22.468	0.967	0.0096	19.015	0.997	18.22
	200	0.109	25.474	0.960	0.0087	25.250	0.998	24.40

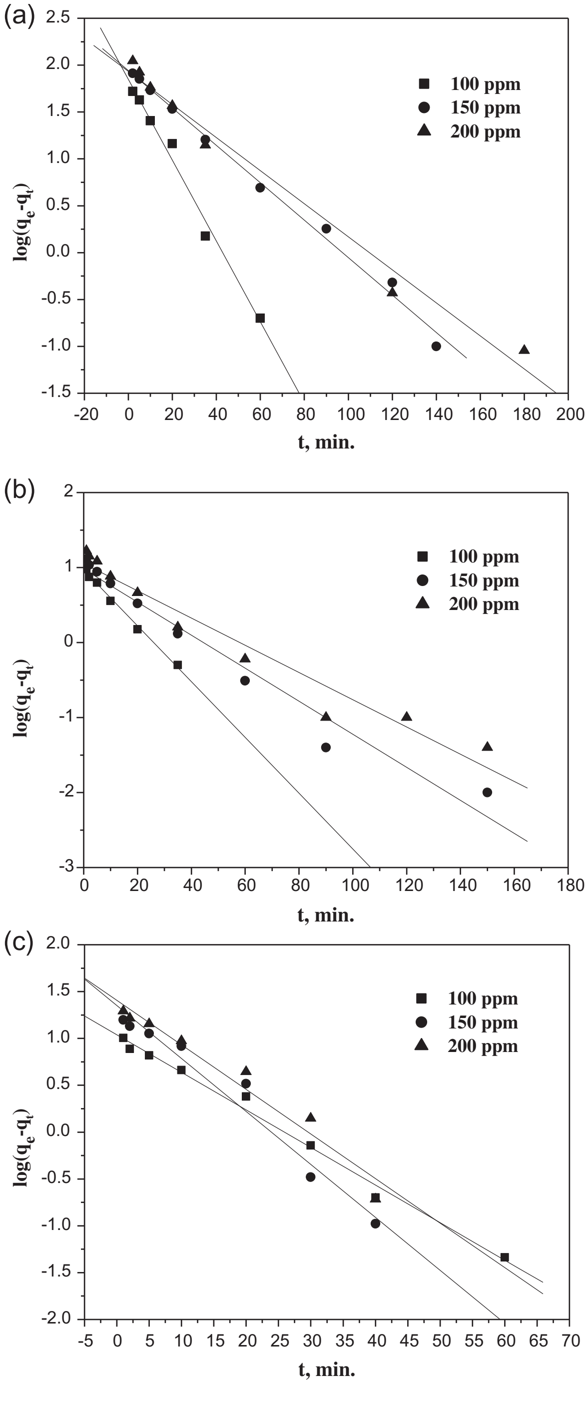

Fig. 6. Pseudo-first-order reaction kinetics for the sorption of NGB by charcoal (a), kaolinite (b), and tafla (c).

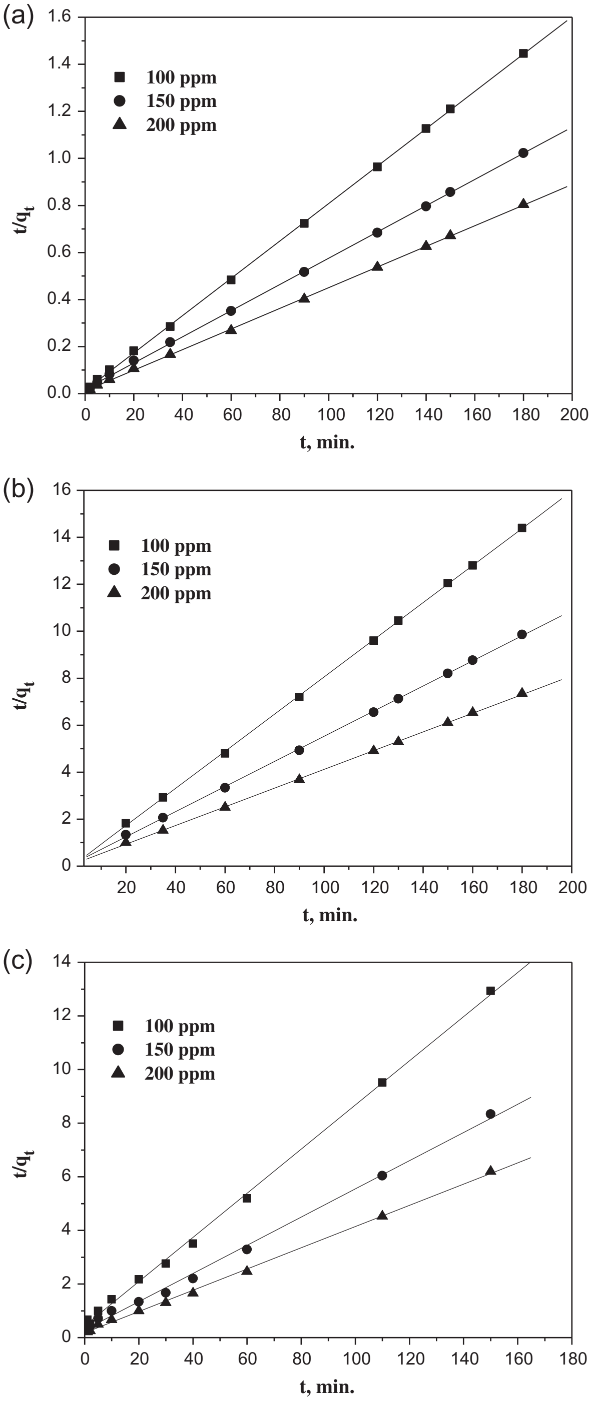

Fig. 7. Pseudo-second-order reaction kinetics for the sorption of NGB by charcoal (a), kaolinite (b), and tafla (c).

3.4. Sorption equilibrium isotherm and process design

Sorption isotherms are fundamental in describing the interactive behavior between the sorbate molecules or ions species and solid-phase sorbents, and are important for investigating mechanisms of sorption [11]. Analysis of equilibrium data is important to develop an equation that accurately represents the results and could be used for design purposes [11,22]. Isotherms are mathematical models based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of solid-phase sorbents, the type of coverage, and the possibility of interaction between the sorbate molecules. Isotherms are employed to establish the maximum capacity of sorption of target species on sorbents, which is expressed in terms of quantity of NGB adsorbed per unit of mass of adsorbent used (mg/g) [23,24].

In this investigation, the adsorption isotherms for the NGB removed were studied using initial concentration of NGB between 100 and 200 mg l^{-1} at an adsorbent dosage of 0.01 g charcoal at pH 6 and 0.1 g kaolinite and tafla at pH 4. The equilibrium data obtained were then fitted to the Langmuir and Freundlich adsorption isotherm models.

The Langmuir sorption isotherm has been widely used to describe sorption phenomena from solution using solid-phase adsorbents. The model assumes that the uptake of molecules or metal ions occur on a homogenous surface by monolayer without any interaction between adsorbed molecules. The Langmuir isotherm is represented by the following equation [11,22–24].

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ}\left(\frac{1}{C_e}\right) \tag{11}$$

where C_e is the equilibrium concentration (mg/l), q_e is the amount of NGB dye (mg/g) at equilibrium, Q is the theoretical monolayer capacity, and b is the sorption equilibrium constant related to the energy of sorption.

The linear plots of $1/C_e$ against $1/q_e$ show that sorption of NGB obeys Langmuir sorption model. A straight line was obtained (figure not shown, we took the results for the sake of brevity) with high correlation coefficient confirming that Langmuir isotherm is applicable for sorption of NGB dye onto charcoal, kaolinite, and tafla. From the slope and intercept, one can determine the values of sorption equilibrium constant, b and the monolayer capacity, Q. One of the essential characteristics of Langmuir isotherm model can be expressed in terms of a dimensionless constant [22–24] called separation factor or equilibrium parameter, R_L, which can be calculated from Langmuir constant, b, as the following:

$$R_L = \frac{1}{1 + bC_0} \tag{12}$$

where b is a Langmuir constant and C_0 is the initial concentration of NGB dye. The value of R_L indicates the type of isotherm to be irreversible if, $R_L = 0$, favorable $0 < R_L < 1$, linear $R_L = 1$, or unfavorable $R_L > 1$. The R_L values for the adsorption of NGB dye on different adsorbents are listed in Table 3. The data obtained represent a favorable adsorption for all the adsorbents under study.

The Freundlich equation is an empirical equation based on sorption on a heterogeneous surface (the model assumes that different sites with several sorption energies are involved) and properly represents the sorption data at low and intermediate concentrations on heterogeneous surfaces. The model has the following form [11,22–24]:

$$\log q_e = \log k + \frac{1}{n} \log C_e \tag{13}$$

where C_e is the equilibrium concentration (mg/l), n and K are constants which depend on the nature of the adsorbate, adsorbent, and temperature. The plot of log q_e vs. log C_e yields a straight line, which confirms the Freundlich isotherm model for sorption (we took the results for the sake of brevity). The Freundlich constants $1/n$ and k can be determined from the slope and the intercept, respectively, as illustrated in Table 3.

The correlation coefficient for the Freundlich plot was found to be 0.9996 and 0.982 for charcoal and tafla, indicating a better fit for the experimental data compared to Langmuir plot. The adsorption of NGB dye by charcoal and tafla obeys the Freundlich isotherm with high correlation coefficient. In the case of

Table 3
Langmuir and Freundlich parameters for sorption of NGB dye onto charcoal, kaolinite, and tafla

	Langmuir parameters				Freundlich parameters		
Adsorbent	Q (mg g^{-1})	R_L	b (l mg^{-1})	R^2	K (mg g^{-1})	$1/n$	R^2
Charcoal	232.56	0.0109	0.452	0.971	95.22	0.2803	0.9996
Kaolinite	25.80	0.0043	1.181	0.901	13.40	0.352	0.866
Tafla	23.86	0.0041	1.226	0.944	12.701	0.285	0.982

kaolinite, the sorption obeys the Langmuir isotherm with high correlation coefficient of 0.901, Table 3.

3.5. Effect of temperature and thermodynamic parameters

The temperature has two major effects on the sorption process [11]. Increasing the temperature is known to increase the rate of diffusion of the sorbate molecules across the external boundary layer and in the internal pores of the sorbent particle, owing to the decrease in the velocity of the solution. In addition, changing the temperature will change the equilibrium capacity of the sorbent for a particular sorbate [23].

The plot of sorption capacity as a function of temperature shows an increasing amount of sorbed NGB dye with increasing in temperature from 25 to 50˚C, indicating that the adsorption is an endothermic process, Fig. 8. The enhancement of sorption capacity of the adsorbents at higher temperatures was attributed to the enlargement of pore size and activation of the sorbent surface [11].

The temperature dependence of the sorption process is associated with changes in several thermodynamic parameters. These parameters are very important because they give information about the spontaneity of the sorption processes. Parameters, such as Gibbs free energy, ΔG°, enthalpy, ΔH°, and entropy changes, ΔS°, for the sorption of NGB dye onto charcoal, kaolinite, and tafla can be calculated using the following relations [23]:

$$\Delta G^\circ = -RT\ln K_d \tag{14}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{15}$$

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^\circ}{2.303R} + \frac{-\Delta H^\circ}{2.303R}\frac{1}{T} \tag{16}$$

where K_d is the distribution coefficient, $K_d = q_e/C_e$ (l/g), R is the general gas constant (R = 8.314 J mol^{-1} K), and T is the absolute temperature (K). The relation between log K_d and $1/T$ is given in Fig. 9 as a linear relation; the values of enthalpy change and entropy change can be calculated from the slope and intercept of the line, respectively. The values of these parameters are listed in Table 4.

The obtained negative values of the free energy change, ΔG°, confirm that sorption of NGB dye onto three adsorbents is spontaneous and thermodynamically favorable process [22]. The positive values of ΔH° confirm the endothermic nature of the adsorption process [22]. The positive values of ΔS° show the increased disorder and randomness at the solid/solution interface of NGB dye with the three adsorbents [24]. The uptake of NGB dye showed to be most efficient at a temperature of 333 K.

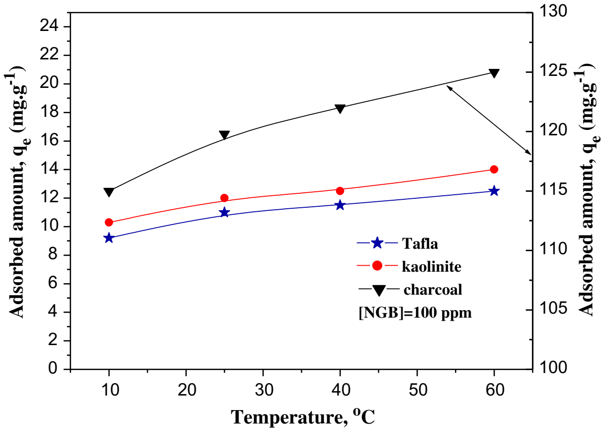

Fig. 8. Effect of temperature on the uptake of NGB dye.

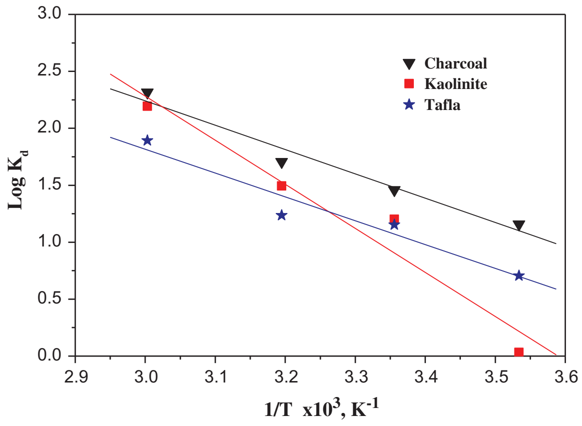

Fig. 9. Van't Hoff plot for sorption of NGB onto charcoal, kaolinite, and tafla.

3.6. Comparison with other adsorbents

There are very limited papers on the sorption of naphthol green B dye in the literature. The sorption capacities of charcoal, kaolinite, and tafla have been compared with other sorbents reported in the literature as having been examined for the removal of NGB dye under similar conditions to those employed in the present work. These have been presented in Table 5. The tabulated data show that charcoal, kaolinite, and tafla exhibit considerably higher adsorption capacity.

Table 4
Thermodynamic parameters for sorption of NGB dye

Sorbent	Temp. (K)	K_d (l g^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K)	ΔG° (kJ mol^{-1})
Charcoal	283	14.375	40.87	165.51	−6.273
	292	28.798			−8.327
	313	50.833			−10.225
	333	207.37			−14.772
Kaolinite	283	1.077	74.07	265.9	−0.175
	298	15.901			−6.855
	313	31.125			−8.948
	333	156.13			−13.99
Tafla	283	5.083	40.10	154.99	−3.826
	298	14.243			−6.582
	313	17.236			−7.410
	333	78.00			−12.064

Table 5
Comparison of $q_{\max}$ for various sorbents

Adsorbent	Q_m (mg g^{-1})	References
Charcoal	232.56	Present study
Kaolinite	25.80	Present study
Tafla	23.86	Present study
MHS	10.0	[4]
Mg/Al-LDO	215.2	[25]

Notes: MHS is metal hydroxide sludge (industrial by product). Mg/Al is Calcined layered double hydroxides (prepared material).

4. Conclusions

This study focused on treating wastewater to remove dye by sorption onto natural clays and commercial products. Charcoal, kaolinite, and tafla were selected to be tested as sorption materials. The sorption is highly dependent on the initial concentration of NGB dye. The attractive features of these adsorbents are that they are environmentally friendly, effective, and of low cost. Charcoal, kaolinite, and tafla have proven to be the promising materials for the removal of contaminants from aqueous phase. The maximum removal capacity of charcoal was found to be greater than that of kaolinite and tafla. The obtained results could be used for designing a plant for treatment of metal complex dyes or organic pollutant-rich water and wastewater economically.

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