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Assessment of the adsorptive color removal of methylene blue dye from water by activated carbon sorbent-immobilized-sodium decyl sulfate surfactant

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ABSTRACT

Sodium decyl sulfate (SDeS) as an anionic surfactant was used for the surface modification of activated carbon (AC). Micelle-like structure was formed on the surface of AC sorbent-modified surfactant (AC-SDeS). The modified sorbent was characterized by Fourier transform infrared spectroscopy, scanning electron microscopy and thermal gravimetric analysis. The AC-SDeS sorbent was proved to have high enhanced removal capability for methylene blue (MB), a cationic dye, from various water matrices. The adsorptive removal process of MB dye was investigated and monitored using the batch equilibrium technique. Adsorptive removal of MB dye by AC-SDeS sorbent was examined in presence of various controlling parameters such as pH, contact time, sorbent dosage, initial dye concentration, and different interfering substances. The results showed that the optimum pH range for removal of MB dye from aqueous solutions (120 mg L^{-1}) is pH 7.0–13.0 and the determined percentage values of removal were 92.25–94.50%. The percentage of dye removal decreased upon increasing the initial dye concentration and addition of interfering substances. The Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich adsorption models were applied to describe the equilibrium isotherms, and the experimental data were found to agree with the Langmuir isotherm model. The pseudo first-order, pseudo-second-order, intraparticle diffusion and Elovich kinetic models were used to examine the kinetic data and determine the rate constants. The results were found to fit well with the pseudo-second-order kinetic model. The efficiency of AC-SDeS for adsorptive removal of MB dye from tap water and real wastewater was also studied and excellent results were obtained as 95.90–96.20 ± 2.0–4.0%.

Keywords: Activated carbon; Color removal; Methylene blue; Sodium decyl sulfate; Wastewater

1. Introduction

Industrial wastewaters contaminated with dyes are generally produced from different industrial sectors including textiles, dyestuff manufacturing, dyeing, and printing. Industrial wastewater containing dye pigments or components can cause severe water pollution problems. The discharge of industrial wastewater containing dye effluents is now becoming an

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environmental problem due to the major concern about the high toxicity of most dyestuffs. In addition to their toxicity, dyes are considered a major contributor to the consumption of dissolved oxygen which is required by aquatic life, reduced light penetration as well as the produced toxicity from heavy metals associated with some pigments or dyes [1].

Several well-known treatment methods can be used to overcome and minimize the major problems associated with the dye pollution. These include physical processes such as filtration or membrane separation, chemical treatments such as chemical oxidation or coagulation and biological remediation such as microbial degradation [2]. However, these outlined processes have their limitations such as high cost, generation of secondary pollutants, and low removal efficiency. However, adsorption has been found as the most promising and convenient method in industrial wastewater treatments of dyes or pigments [3,4]. Adsorption is also known as the most effective economic and preferred procedure due to its convenience, ease of operation, simplicity of design, initial low cost, and insensitivity to toxic pollutants [5–7]. The adsorption process does not also result in the formation of harmful substances such as other methods [8]. Natural adsorbents, including clay and zeolite, are known as natural scavenger for adsorption and removal of different types of pollutants such as dyestuffs and heavy metals from wastewater due to their high cation-exchange capacity and surface area [9]. In addition, other types of effective adsorbents for removal of coloring materials from aqueous effluents are mainly based on the application of high surface area, pore volume as well as inert properties, and high adsorption capacity of activated carbon (AC) which is produced from different agricultural components [10].

Recently, removal of organic contaminants using loaded surfactants on solid surface has drawn much attention. Methylene blue (MB), a cationic dye, and orange II (OII), an anionic dye, in wastewater were removed by unmodified and zeolite-modified surfactant using a batch equilibration method [9]. The effect of cationic surfactant was studied to remove reactive black 5 (RB5) dye using cetylpyridinium chloride (CPC) by pure AC, AC in CPC solution, and precoated AC by CPC [11]. The biosorption of MB onto dried *Rhizopus arrhizus*, a filamentous fungus, was examined in the absence and presence of increasing concentrations of sodium dodecyl sulfate [12]. Rarasaponin that belongs to the natural surfactant was used as modifying agent for preparation of organo-bentonite and used for batch adsorption capability of MB from aqueous solution [13]. Activated carbon-immobilized cationic surfactant was designed to enhance the decolorization behavior of RB5, as an anionic dye, from aqueous and industrial wastewater samples in presence of various controlling experimental conditions [14].

The present work aims to perform an assessment study to evaluate the efficiency of enhanced adsorptive removal of MB, as a cationic dye, from various water matrices using micelle-like structures based on the immobilization of sodium decyl sulfate (SDeS), as anionic surfactants, on the surface of activated carbon sorbent (AC-SDeS). Batch studies were carried out involving optimization of the process parameters such as pH, contact time, adsorbent dosage, initial dye concentration, and effect of interfering species. Equilibrium studies and kinetic analysis as well as the potential application for removal of MB were also aimed.

2. Materials and methods

2.1. Materials

Analytical grade chemicals and reagents were purchased and used without further purification. Commercial AC powder was purchased from Adwic Chemicals, Egypt and used as received. MB dye (basic blue 9) was purchased from Mumbai, India and a stock solution was prepared by dissolving 1.0 g in 1.0 L of double distilled water (DDW). The stock solution was successively diluted to prepare fresh solutions of the desired concentrations at the start of each experiment. The anionic surfactant, SDeS, was supplied by Sigma-Aldrich with 99.9% purity. The chemical structures of MB dye and the general characteristics of the dye and surfactant are summarized in Table 1.

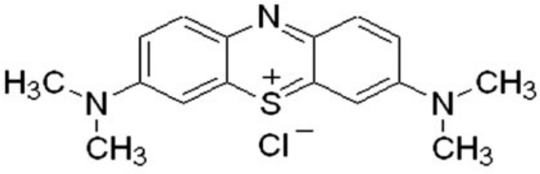
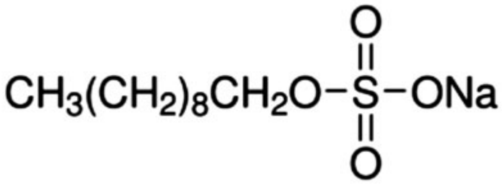
2.2. Preparation of AC-modified-surfactant

A solution containing 20.0 mmol of SDeS in 60.0 mL of ethanol was prepared and 10.0 g of AC sorbent was then added. The reaction mixture was refluxed for 4 h and the modified AC sorbent (AC-SDeS) was then separated from the solvent by filtration and washed with ethanol several times to remove superficially retained surfactant. Finally, the modified AC sorbent was dried in an oven at 60°C for 3 h and stored in an airtight glass container.

2.3. Instrumentations

A digital pH meter (CRISON) was calibrated using standard buffer solutions of pH 4.0 and 9.2 and used for the pH measurement. The rate of decolorization

Table 1
General characteristics of MB and SDeS

Compound	General specifications	Molecular weight (g mol^{-1})	Structure
Methylene blue	Color index: 52,015 λ_{max}: 664 nm	319.85	 $C_{16}H_{18}N_3SCl$ (319.85 g/mol)
SDeS	Name: Sodium decyl sulfate (SDeS)	260.33	 $CH_3(CH_2)_8CH_2O-S(=O)_2-ONa$ $C_{10}H_{21}O_4SNa$

and dye removal were recorded with respect to the change in the intensity of absorption peak at (λ_{max} = 664 nm) using double beam UV–visible spectrophotometer (JASCO V-530 UV–Vis). The light sources used in the V-530 are deuterium (D2) lamp (190–350 nm) and halogen (WI) lamp (340–1,100 nm) in the VIS–NIR region. Fourier transform infrared (FT-IR) spectrum of AC-SDeS sorbent was recorded in the transmission mode at room temperature on a BRUKER Tensor 37 Fourier transform infrared spectrophotometer in the range of 400–4,500 cm^{-1} using KBr pellet technique. Scanning electron microscope (JSM-6360LA, JEOL Ltd.), (JSM-5300, JEOL Ltd.) and an ion-sputtering coating device (JEOL-JFC-1100E) were used to examine the surface morphology of the AC, AC-SDeS, and AC-SDeS-bound-MB sorbents. Scanning electron microscopy (SEM) specimens were coated with gold to increase the conductivity. Thermal gravimetric analysis (TGA) and thermoanalytical curves were measured using a Perkin–Elmer TGA7 Thermobalance. The selected operating conditions are: temperature heating range = 20–600˚C, heating rate = 10˚C min^{-1}, and flow rate = 20 mL min^{-1} of pure nitrogen atmosphere and the sample was taken in the range of 5.0–6.0 mg.

2.4. Adsorption studies

The adsorption characteristics of modified AC sorbent, AC-SDeS for removal of MB from aqueous solutions were studied using the batch equilibrium technique under various experimental controlling parameters such as pH, contact time, sorbent dosage, initial dye concentration, and interfering species. The batch experiments were carried out using an automatic shaker agitated with speed of 150 rpm at 25 ± 1˚C. Different concentrations of MB dye were prepared in DDW.

Experiments were carried out to evaluate the effect of pH on the adsorptive removal process of MB dye by AC-SDeS sorbent according to the following procedure. Twenty milliliter of 60.0–200.0 mg L^{-1} initial concentration of dye solutions was adjusted to the required pH value (pH 1.0–11.0) using 1.0 M-HCl or 1.0 M-NaOH. A 10.0 ± 1.0 mg sample of AC-SDeS sorbent was added to the above dye solution and automatically shaken for 10.0 min. After equilibration, the dye solution was filtered and the remaining concentration of dye was detected by measuring the absorbance value at λ_{max} = 664 nm.

The effect of sorption equilibrium time was studied using 20.0 mL solution of the dye, initial concentration in the range of 60.0–200.0 mg L^{-1}, and the AC-SDeS sorbent dosage was taken as 10.0 ± 1.0 mg. The pH of the dye solution was adjusted to pH 7.0 and the shaking time values were varied from 0.0 to 20.0 min. The unextracted MB dye was filtered and the absorbance was measured at the specified λ_{max}.

The effect of sorbent dosage on the adsorptive removal of MB dye was performed by a similar batch experiment in which a 20.0 mL solution of the dye was used. The initial concentration of MB was taken in the range of 60.0–200.0 mg L^{-1} and the selected sorbent dosage was used in the range of 5.0–25.0 ± 1.0 mg. A shaking time of 10 min and pH 7.0 were selected as the optimum conditions. After equilibration, the dye solution was filtered and the absorbance value of unextracted dye was measured at λ_{max} = 664 nm.

The effect of different interfering species such as NaCl, KCl, Na_2SO_4, and $MgSO_4 \cdot 7H_2O$ was studied using a 20.0 mL of the dye solution at different initial concentrations of MB dye (60.0–200.0 mg L^{-1}). A 30.0 ± 1.0 mg dosage of the different interfering salts was mixed with the dye solution and the pH value of the solution was adjusted to 7.0. This mixture was automatically shaken in presence of 12.0 ± 1.0 mg of the AC-SDeS sorbent for 10 min. After equilibration, the dye solution was filtered and the absorbance value of unretained dye solution was measured at λ_{max} = 664 nm.

Finally, the effect of initial dye concentration on the adsorptive removal of MB dye by AC-SDeS sorbent was studied using different dye concentrations in the range of 50.0–200.0 ± 1.0 mg L^{-1}. A 20.0 mL solution of the MB dye was added to 12.0 ± 1.0 mg AC-SDeS sorbents. The pH value of these solutions was adjusted to 7.0 and the reaction mixtures were automatically shaken for 10 min. The procedure was then completed as described above.

The potential applications of AC-SDeS sorbent for adsorptive removal of MB dye from real tap water and wastewater samples were accomplished according to the following procedures: the MB dye was spiked in 50.0 mL of water sample to establish dye concentration values of 60.0 and 125.0 mg L^{-1} in the aqueous solutions. The water samples were adjusted to the optimum pH 7.0 and 12.0 ± 1.0 mg of AC-SDeS sorbent was then added. The samples were automatically shaken for 10 min and the absorbance of the final dye concentration was measured after filtration at λ_{max} = 664 nm. Blank water samples were also prepared and used for comparison. Dilutions were made when the absorbance measurement exceeded the linearity of the calibration curve.

3. Results and discussion

3.1. Characterization of modified AC-SDeS sorbent

Several instrumental techniques were used to investigate the surface modification of AC sorbent including FT-IR, SEM, and TGA.

3.1.1. FT-IR characterization

The FT-IR spectra of free AC, AC-SDeS, and AC-SDeS-bound-MB sorbents are shown in Fig. 1(a)–(c), respectively. The AC sorbent was characterized by the presence of a series of peaks at 3,422 cm^{-1} owing to $\nu_{O–H}$, 2,914 cm^{-1} assigned to n(C–H) from methyl and methylene groups, 1,630 cm^{-1} due to $\nu_{C=O}$ from carboxylate group, 1,372 cm^{-1} of $\nu_{C–H}$ from methyl groups and the peaks at 610–1,000 cm^{-1} may be related to the $\nu_{=C–H}$ of alkenes [15]. It is clear from these peaks that the AC sorbent has a good number of functional groups. Most probably, these functional groups are responsible for adsorption of the adsorbate molecules. However, the FT-IR spectra of AC-SDeS and AC-SDeS-bound-MB were found to exhibit similar functional groups due to the domination of AC as the major component in these materials. In addition, the anionic surfactant molecules are generally loaded on the AC surface as a result of the electrostatic interaction between the anionic surfactant molecules and the surface of AC [14,15].

3.1.2. SEM characterization

The scanning electron microscopic image of AC sorbent is shown in Fig. 2(a) and clearly indicates the existence of AC sorbent in aggregated irregular surfaces with a large number of micropores of various sizes on the surface [14,15]. Fig. 2(b) shows the SEM images of AC-SDeS sorbent and this image indicates also that the distribution of surfactant particles on AC sorbent produced a smoother surface and maintained good porosity in the modified AC-SDeS sorbent. On the other hand, adsorption of MB dye on the surface of AC-SDeS sorbent was also characterized by SEM imaging as represented in Fig. 2(c). Smoother and brighter surface of AC-SDeS-bound-MB was also evident. This may be due to the possible chemical reaction of anionic surfactant with the cationic dye molecule for the formation of a complex species.

3.1.3. Thermal gravimetric analysis

Thermal gravimetric analysis of AC, AC-SDeS, and AC-SDeS-bound-MB were studied in the heating range of 20–600˚C and the results of this study are shown in Fig. 3(a)–(c). The TGA of AC sorbent shown in Fig. 3(a) was characterized by the formation of two thermal degradation steps at temperature ranges 24.60–93.15 and 486.12–598.68˚C. The first decomposition step corresponds to a percentage loss of 26.54% and it is mainly related to the thermal desorption of adsorbed water molecules from the surface of

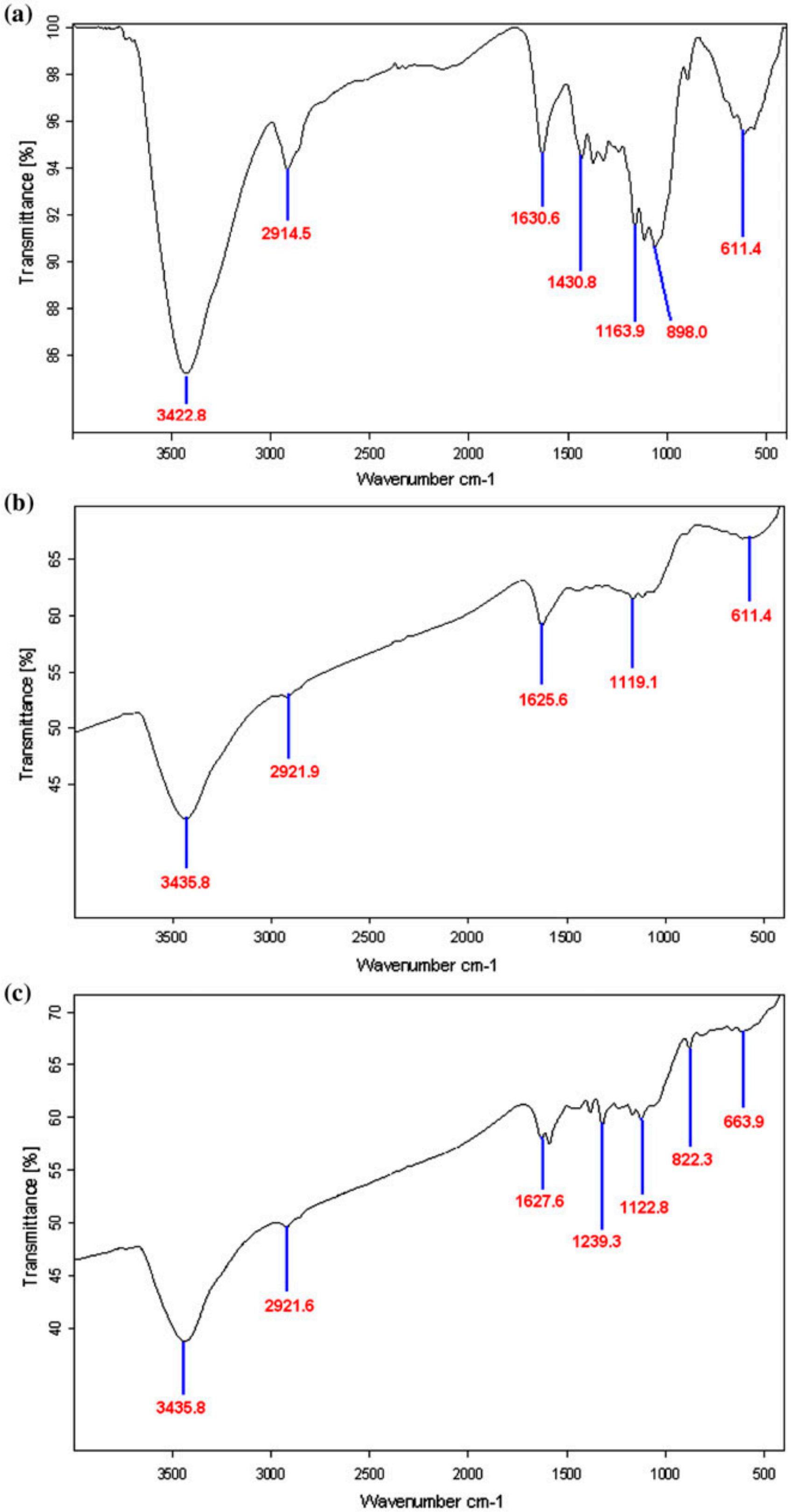


Fig. 1. FT-IR spectra of various AC-materials. (a) FT-IR of AC, (b) FT-IR of AC-SDeS, and (c) FT-IR of AC-SDeS-bound-MB.

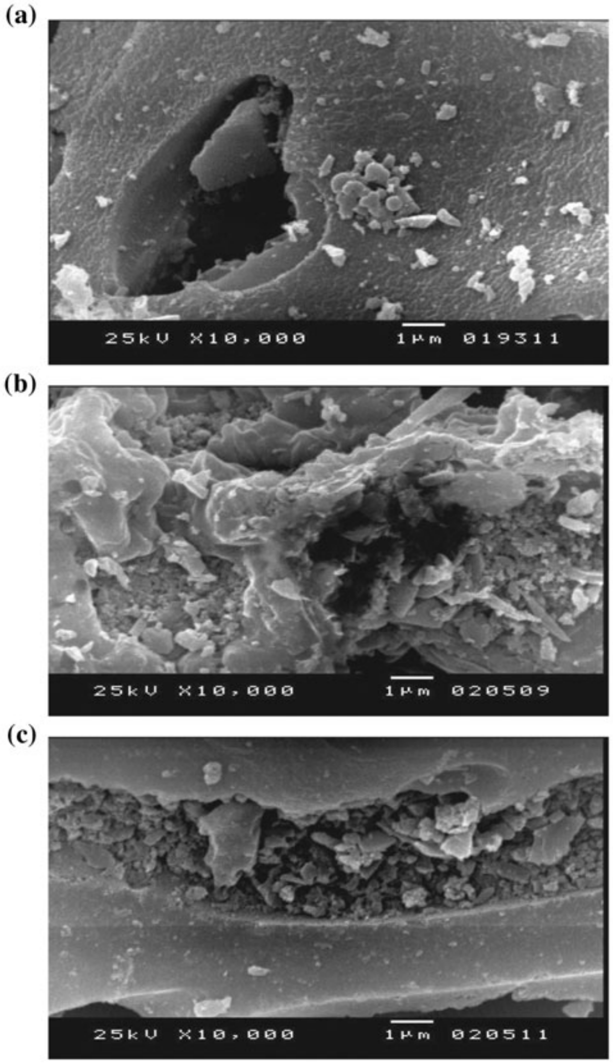


Fig. 2. SEM images of various AC-materials. (a) SEM-image of AC, (b) SEM-image of AC-SDeS, and (c) SEM-image of AC-SDeS-bound-MB.

AC-sorbent. The second degradation step is represented by a percentage loss corresponding to 20.21% and it is suggested to take place by partial decomposition of the surface-loaded organic functional groups as well as some decomposed skeleton carbon atoms [14,15]. On the other hand, immobilization of SDeS on the surface of AC for the formation of AC-SDeS-sorbent was found to exhibit a different thermal behavior as shown in Fig. 3(b) and the TGA of AC-SDeS-bound-MB is shown in Fig. 3(c). The TGA of AC-SDeS sorbent was characterized by producing two similar degradation steps at 29.14–100.81 and 473.40–599.56˚C with the mass losses corresponding to 15.98 and 13.27, respectively. A similar trend was also identified in the TGA of the AC-SDeS-bound-MB (Fig. 3(c)). This behavior refers to the higher thermal stability characteristics of these two materials. The thermal decomposition temperature ranges and the percentage of mass losses of all degradation steps are compiled in Table 2.

3.2. Sorption of MB dye by AC-SDeS sorbent

The amounts of adsorbed dye at equilibrium and the percentage removal values of dye from solution were calculated according to Eqs. (1) and (2), respectively.

$$q_e = \frac{C_o - C_e}{W/V} \tag{1}$$

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

where C_o and C_e are the initial and equilibrium concentrations of MB dye in solution expressed in mg L^{-1}, V is the volume of MB solution in L, W is the weight of AC-SDeS sorbent in g, and q_e is the amount of MB dye per sorbent mass.

3.2.1. Effect of pH on the adsorptive removal of MB dye by AC-SDeS sorbent

The pH value of the adsorbate solution is an important controlling parameter in the adsorption and removal processes. Generally, the adsorbate solution is highly influenced by the initial pH value compared to the final pH. The effect of pH on the percentage removal of MB dye from aqueous solution was studied by varying the initial pH value of the dye solution and the results are illustrated in Fig. 4. It is observed for all dye concentration values that the percentage removal of dye increased by the pH increase from 1.0 to 11.0 using the modified AC-loaded surfactant, AC-SDeS. However, the value of pH 7.0 may be taken as the optimum one for removal of MB dye from aqueous solutions. The pH_{pzc} value of AC-SDeS sorbent was also identified from Fig. 5, as previously reported [16], and found to be 6.90. Two possible suggested mechanisms for dye adsorption may be outlined [14]. (i) The electrostatic interaction between the sorbent and the dye molecule. (ii) The direct chemical reaction between the dye and sorbent. In presence of pH 1.0, the hydrogen ion concentration is high and the surface of AC-SDeS sorbent acquired positive charges by absorbing H^+ ions. As the modified carbon surface is positively charged at low pH, a significantly high electrostatic repulsion exists between these

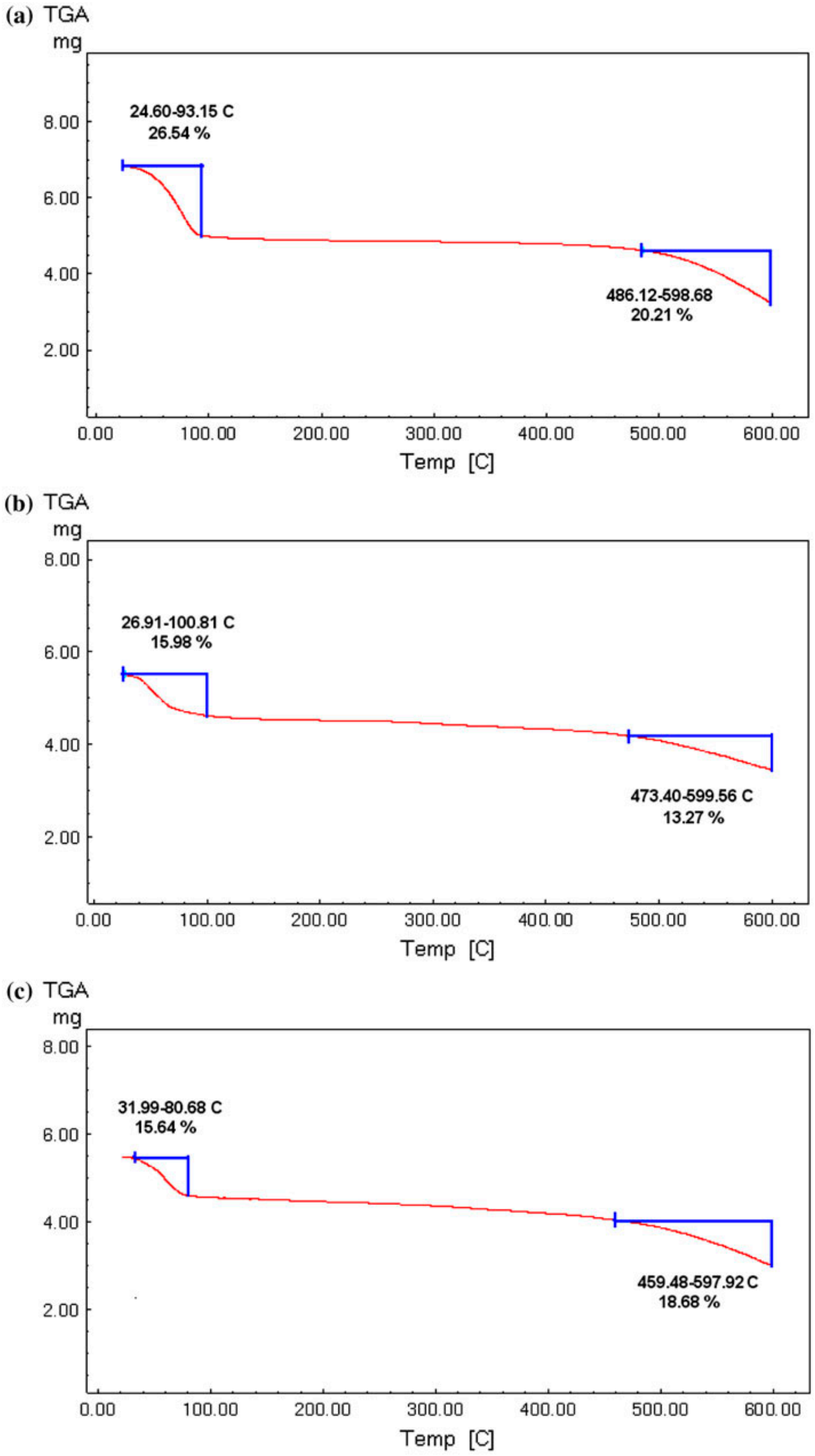


Fig. 3. TGA thermograms of various AC-materials. (a) TGA of AC, (b) TGA of AC-SDeS, and (c) TGA of AC-SDeS-bound-MB.

Table 2
TGA data of various AC sorbents

Adsorbent	Decomposition step (˚C)	Loss (%)	Desorbed species
AC	First: 24.60–93.15	26.54	Desorbed water molecules
	Second: 486.12–598.68	20.21	Decomposed surface groups of AC
AC-SDeD	First: 26.91–100.81	15.98	Desorbed water molecules
	Second: 473.40–599.56	13.27	Decomposed surface groups of AC
AC-SDeS-MB dye	First: 31.99–80.68	15.64	Desorbed water molecules
	Second: 459.48.40–597.92	18.67	Decomposed surface groups of AC

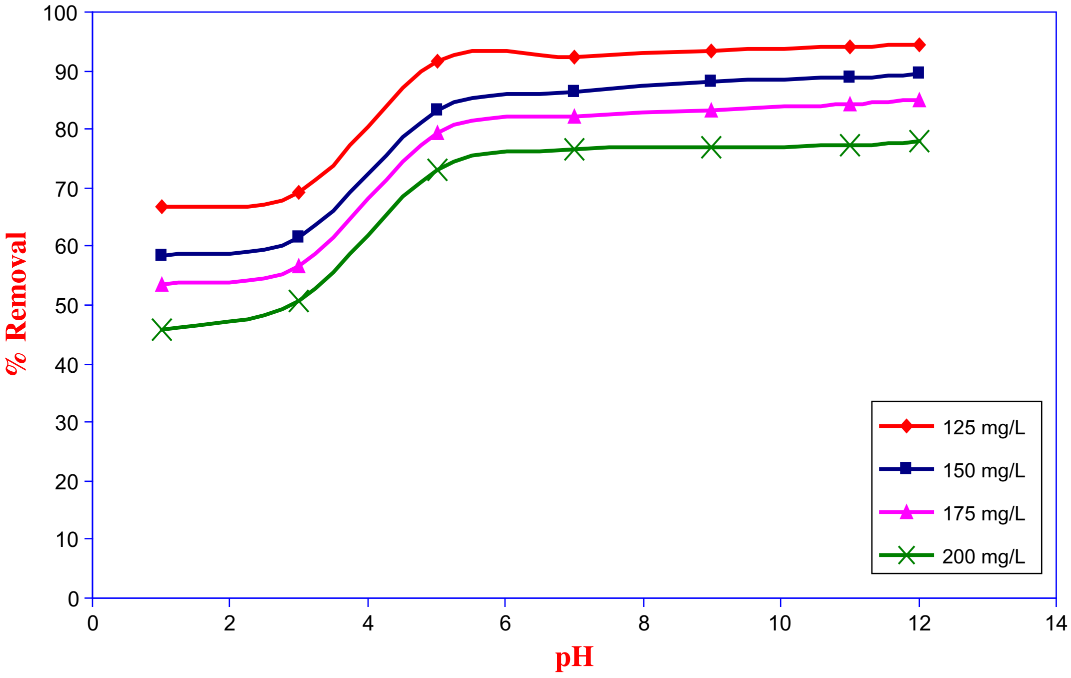


Fig. 4. Effect of pH on MB dye removal by AC-SD.

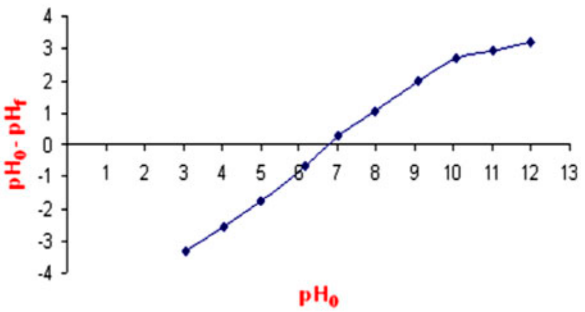


Fig. 5. Variation of (pH_0–pH_f) vs. initial pH_0.

charges and cationic MB molecule [15]. This leads to a minimum efficiency in dye removal as determined by AC-SDeS sorbent in the range of 45.93–66.93%. As the pH value of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. Negatively charged surface sites on the surfactant modified carbon favor the adsorption of dye cations due to the electrostatic attraction. The value of pH 7.0 was characterized as the most effective one to use in further studies. A similar behavior was observed for MB adsorption by other adsorbents [17,18].

3.2.2. *Effect of contact time on the adsorptive removal of MB dye by AC-SDeS sorbent*

The effect of contact time on the percentage removal of MB by AC-SDeS sorbent is represented in Fig. 6. The MB dye was found to rapidly adsorb on

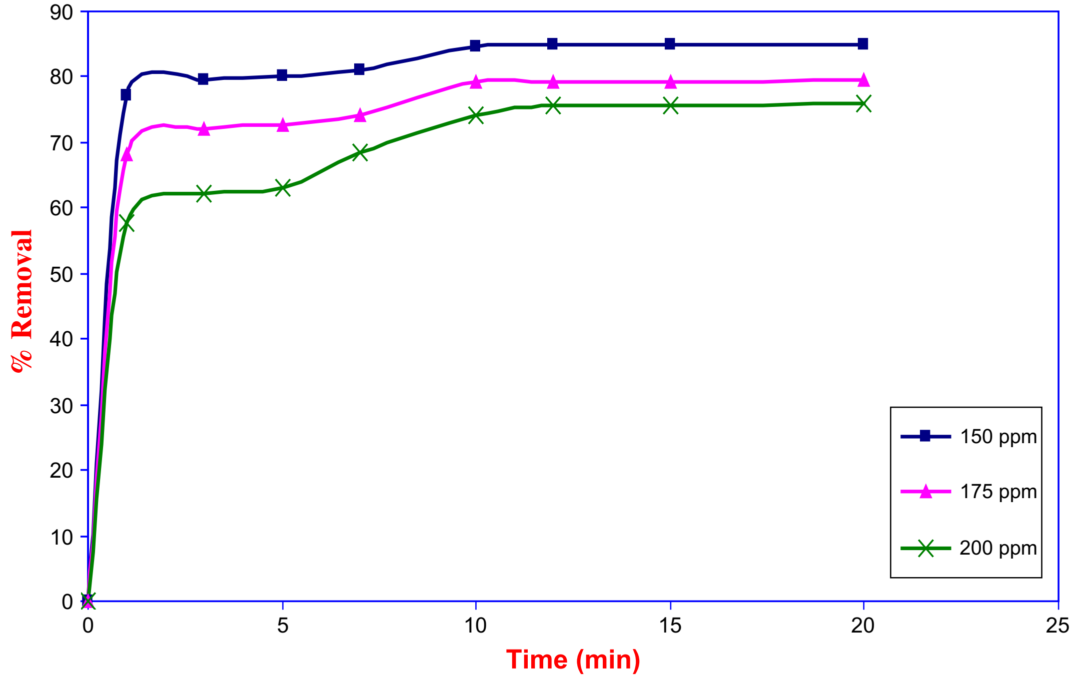


Fig. 6. Effect of contact time on MB dye removal by AC-SDeS.

the surface of AC-SDeS sorbent during the first three min by reaching to the percentage extraction values of 62.14–79.5%. The adsorption rate was found to reach to the equilibrium at about 10 min. At the beginning of this process, the adsorption rate was fast as the dye ions were adsorbed by the exterior surface of the modified AC sorbent as well as due to the abundant availability of active sites on the surface of AC-SDeS sorbent. When the exterior surface reached to the saturation condition, the dye ions extended onto the pores of the sorbent particles and adsorbed by the interior surface of the particles. This phenomenon was characterized by taking a relatively long contact time. A similar trend was also observed for the adsorption of MB by other previously reported adsorbents [19].

3.2.3. *Effect of sorbent dosage on the adsorptive removal of MB dye by AC-SDeS sorbent*

The effect of the sorbent mass on the removal process of MB by AC-SDeS was also studied by increasing the dose at the selected optimum conditions. The results of this study are depicted in Fig. 7 and show that the percentage values of adsorption increased with the increase in the sorbent dosage. This behavior is mainly due to a larger surface area and high availability of more adsorption sites [20]. However, the amount of adsorbed dye per unit weight of adsorbent decreases with the dosage increase. This may be attributed to the presence of low number of MB dye molecules compared to the existence of high surface area of AC-SDeS sorbent [21]. Therefore, the optimum dosage of AC-SDeS sorbent was identified as 12.0 mg/20 mL.

3.2.4. *Effect of interfering species on the adsorptive removal of MB dye by AC-SDeS sorbent*

The effects of different interfering substances such as NaCl, KCl, Na_2SO_4, and $MgSO_4{\cdot}7H_2O$ in the process of adsorptive removal of MB dye from aqueous solutions were examined in different initial concentrations of the dye and the results of this study are compiled in Table 3. The collected results of this study indicate that the addition of an ionic salt to the MB dye solution will lead to a slight decrease in the removal percentage values. Theoretically, when the electrostatic forces between the sorbent surface and adsorbate species were in the form of attraction, as in this system, an increase in the ionic strength will decrease the adsorption capacity. Conversely, when the electrostatic attraction is a repulsive force, an increase in ionic strength will increase the adsorption efficiency as previously described [22]. The experimental data in this study were found to follow these statements. The adsorption of positive charged MB dye

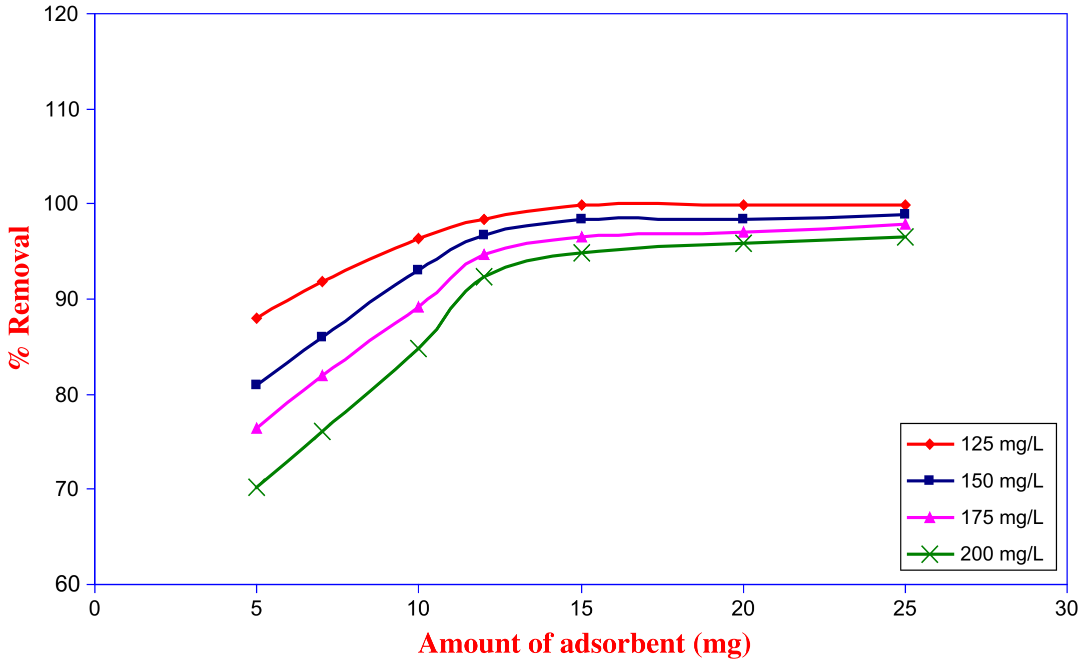


Fig. 7. Effect of adsorbent dosage on MB dye removal by AC-SDeS.

Table 3
Effect of interfering substance on the percent extraction of MB

	Removal percentage of MB dye (%)			
Interfering substance	125 mg L^{-1}	150 mg L^{-1}	175 mg L^{-1}	200 mg L^{-1}
NaCl	96.23	95.42	92.40	90.54
KCl	96.11	95.20	91.73	88.95
Na_2SO_4	94.78	93.90	91.30	87.84
$MgSO_4$	92.50	91.60	86.67	79.29
Free dye	98.90	96.67	94.74	92.40

molecules on negatively charged AC-SDeS sorbent was found to slightly decrease from 98.90–92.40 to 96.23–90.54% upon the addition of NaCl to the dye solution. In this situation, the low concentration levels of Cl^- were found to slightly affect the percentage of MB adsorption on the surface loaded with surfactant molecules. This behavior may be related to the ineffective competitive adsorption interaction of Cl^- with the available sorbent sites. However, the concentration of other ions such as Mg(II) may lead to an increase in the interference at available surface sites of the sorbent through competitive adsorption and hence a decrease in the percentage adsorption and removal of the MB dye is detected as listed in Table 3. This behavior may be interpreted on the basis of ions with smaller hydrated radii which are generally found to increase the swelling capability inside the sorbent pores and thus decrease the affinity of AC-SDeS sorbent for removal of MB dye [23].

3.2.5. Effect of initial dye concentration on the adsorptive removal of MB dye by AC-SDeS sorbent

The influence of initial dye concentration on the adsorption process of MB was investigated using various concentrations at optimum conditions, pH 7.0, 10.0 min shaking time, and 12.0 ± 1.0 mg/20 mL of AC-SDeS sorbent dose and the results of this study are represented in Fig. 8. The efficiency of MB dye removal expressed in percentage values was found to decrease upon increasing the initial concentration of MB dye. This behavior is mainly due to the increased competition for the active sorption sites and this leads to slow down the rate of chemical binding between

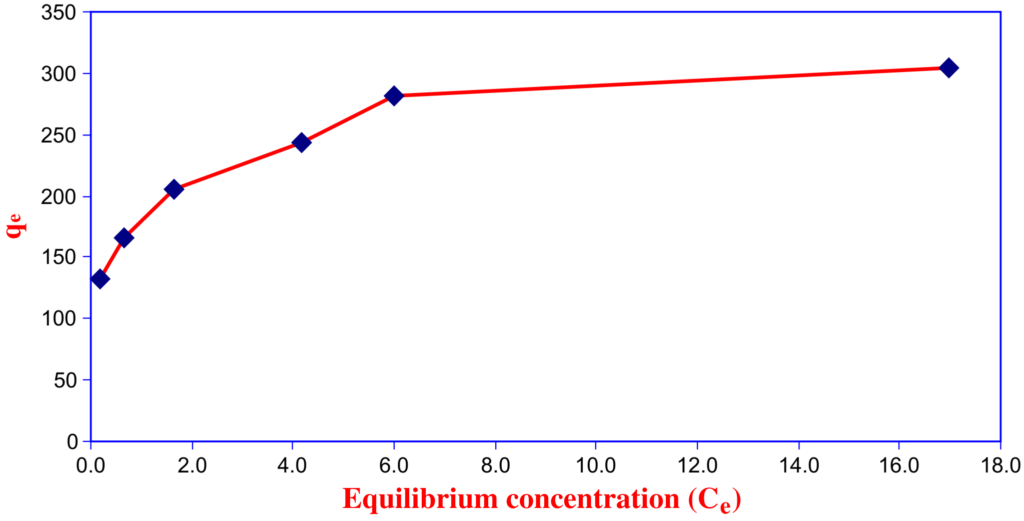


Fig. 8. Effect of initial dye concentration on the MB dye adsorbed at equilibrium by AC-SDeS.

the interacting species. However, the actual amount of removed MB dye per unit mass of AC-modified surfactant sorbent was found to increase with the increase in the initial dye concentration. Such increase is mainly due to the decrease in resistance to the uptake process of dye molecules from its solution. In addition, the increase in initial dye concentration provides an important driving force to overcome the mass transfer resistance of dye between the aqueous and solid surfaces [24].

3.3. Adsorption isotherms

Adsorption isotherms are generally used to evaluate the performance of adsorption process between sorbents and adsorbate. The adsorption models describe the surface properties and affinity of the sorbent. Several adsorption isotherm models are used to describe the binding and interaction behaviors between the adsorbate and sorbents [3,4]. In this study, the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherm models were selected to interpret the experimental data.

Langmuir model assumes that the adsorption process takes place at specific homogenous sites on the sorbent surface without any significant interaction between the adsorbed species. In addition, the adsorption rate is proportional to the number of free sites on the sorbent as well as the fluid concentration. Once an adsorbate molecule occupies a site, no further adsorption process will take place at the same site [25]. The linearized Langmuir adsorption isotherm is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{3}$$

where q_e is the amount of dye adsorbed per unit mass of adsorbent (mg g^{-1}), C_e is the equilibrium concentration of the dye solution (mg L^{-1}), q_m (mg g^{-1}) is the maximum amount of dye per unit weight to form a complete monolayer coverage on the surface, and b (L mg^{-1}) is the Langmuir constant which is related to the affinity of binding sites. The q_m and b terms are computed from the slope and intercept of the straight line of the plot of (C_e/q_e) vs. C_e. Fig. 9 shows the Langmuir adsorption isotherms of MB dye onto the AC-SDeS sorbent. The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless separation factor of the equilibrium parameter (R_L), which is defined by the following equation:

$$R_L = \frac{1}{1 + bC_o} \tag{4}$$

where C_o is the initial concentration of the adsorbate in solution (mg L^{-1}) and b is the Langmuir constant related to adsorption energy (L mg^{-1}). The value of R_L refers to the isotherm type either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [25].

The Freundlich equilibrium isotherm was also used to describe the experimental adsorption data. This isotherm model assumes a heterogenous surface with a non-uniform distribution of adsorption heat

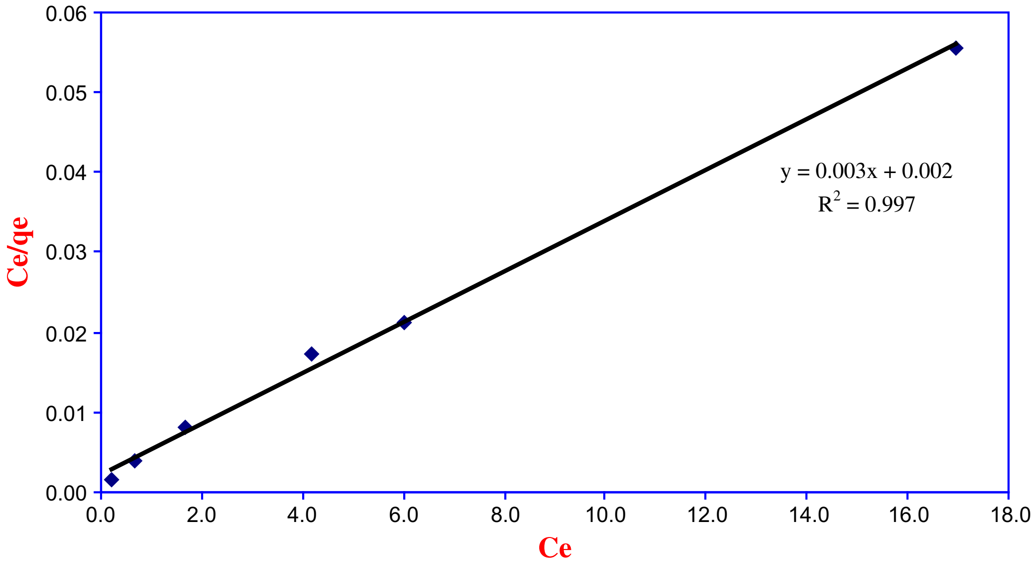


Fig. 9. Langmuir isotherm plot for adsorption of MB onto AC-SDeS sorbent.

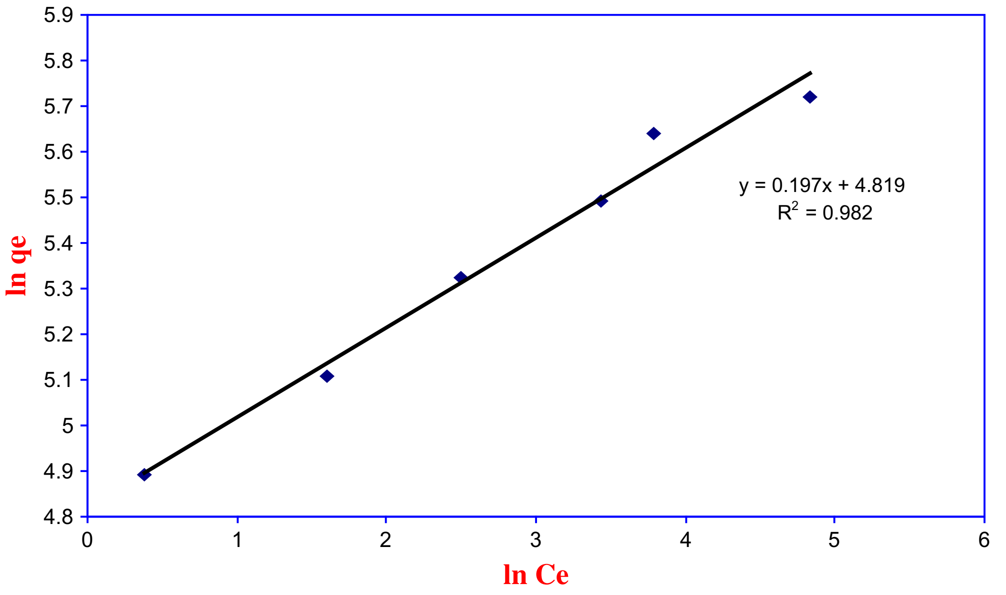


Fig. 10. Freundlich isotherm plots for adsorption of MB dye onto AC-SDeS sorbent.

over the surface. The linearized form of Freundlich isotherm is expressed by the following equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

where K_F and n are the Freundlich constants and these two parameters are related to the adsorption capacity and adsorption intensity of sorbent, respectively. These constants can be obtained from the plot of ln q_e vs. ln C_e. Fig. 10 represents the Freundlich adsorption isotherms of the MB dye onto AC-SDeS sorbent. If the $(1/n)$ slope value is found in the range of 0.0–1.0, it may be assigned as a measure of the adsorption intensity or surface heterogeneity and it is becoming more heterogonous as this value becomes more closer to zero [26].

The Temkin isotherm assumes that the heat of adsorption of all adsorbates increases linearly with the

Table 4
The Langmuir, Freundlich, Temkin, and D–R parameters for adsorption of MB dye by AC-SDeS sorbent

Langmuir parameters				Freundlich parameters		
q_m (mg g^{-1})	b (L mg^{-1})	R_L	R^2	n	K_F (L mg^{-1})	R^2
322.58	1.107	0.0089–0.0044	0.9984	5.1124	55.77	0.9634
Temkin parameters				D–R parameters		
a_T ((L g^{-1})	b_T	B (J mol^{-1})	R^2	q_s (mg g^{-1})	K_{ad} (mol^2 kJ^{-2})	R^2
14.196	60.31	41.08	0.976	249.63	4×10^{-8}	0.73

surface coverage [27]. The linearized form of this isotherm model is given by the following equation:

$$q_e = B \ln a_t + B \ln C_e \tag{6}$$

where q_e is the amount adsorbed at equilibrium in mg g^{-1}, a_T is the Temkin isotherm equilibrium binding constant (L g^{-1}), B is a constant related to heat of sorption (J mol^{-1}) and is calculated from ($B = RT/b_T$), b_T is the Temkin isotherm constant, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature at 298 K. The slopes and intercept obtained from the graphical plot of q_e against ln C_e are used to calculate the Temkin constants as listed in Table 4. The values of $a_T = 14.196$ L g^{-1}, $B = 41.08$ J mol^{-1}, and $b_T = 60.31$ and these indicate that the heat of sorption is mainly related to physical adsorption process [28].

The D–R isotherm is generally applied to express the adsorption mechanism using a Gaussian energy distribution onto a heterogeneous surface. The linear form of the D–R isotherm [29] is given by the following equation:

$$\ln q_e = \ln q_s - (K_{\text{ad}}\varepsilon^2) \tag{7}$$

where q_e is the amount of adsorbate on the adsorbent at equilibrium (mg g^{-1}), q_s is the theoretical isotherm saturation capacity (mg g^{-1}), K_{ad} is the D–R isotherm constant (mol^2 kJ^{-2}), and ε is the polanyi potential which is related to equilibrium and calculated from the following equation:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{8}$$

where R, T, and C_e represent the gas constant (8.314 J mol^{-1} K^{-1}), absolute temperature (K), and adsorbate equilibrium concentration (mg L^{-1}), respectively. The constants such as q_s and K_{ad} were determined from the plot of ln q_e vs ε^2 and q_s was found as 249.635 mg g^{-1} and $K_{\text{ad}} = 4 \times 10^{-8}$ mol^2 kJ^{-2}, respectively, and these values may be also used to account for indicating a physisorption process [29].

Table 4 lists out the identified values and parameters for the adsorption process of MB dye onto AC-SDeS sorbent by the different models. The simple comparison of the correlation coefficients (R^2) of the linearized form of the four evaluated isotherm models indicates that the Langmuir model yields a better fit for the experimental equilibrium adsorption data than the others. The determined q_m was identified as 322.58 mg g^{-1} and this indicates a high adsorption capacity value of MB dye by the newly modified AC-SDeS sorbent. In addition, the characterized R_L values were found in the range of 0.0–1.0 and this again confirms that the Langmuir isotherm was favorable for adsorption of MB on the newly modified AC sorbents.

3.4. Sorption kinetics

The sorption kinetics of MB dye by AC-SDeS describes the dye uptake rate, which in turn governs the residence time of sorption reaction. This study is known as one of the important characteristics in defining the efficiency of sorption. In the present study, the kinetics of MB dye removal was carried out to understand the behavior of this sorbent. The rate constant of adsorption was determined from the pseudo-first-order rate expression given by Lagergren [30] according to the following equation:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \tag{9}$$

where q_e and q_t (mg g^{-1}) are the amounts of adsorbed MB dye at equilibrium and time t (min), respectively. The k_1 (min^{-1}) value is the rate constant of adsorption which is identified from the slope of the plot ln($q_e - q_t$) vs time, as shown in Fig. 11. The determined correlation

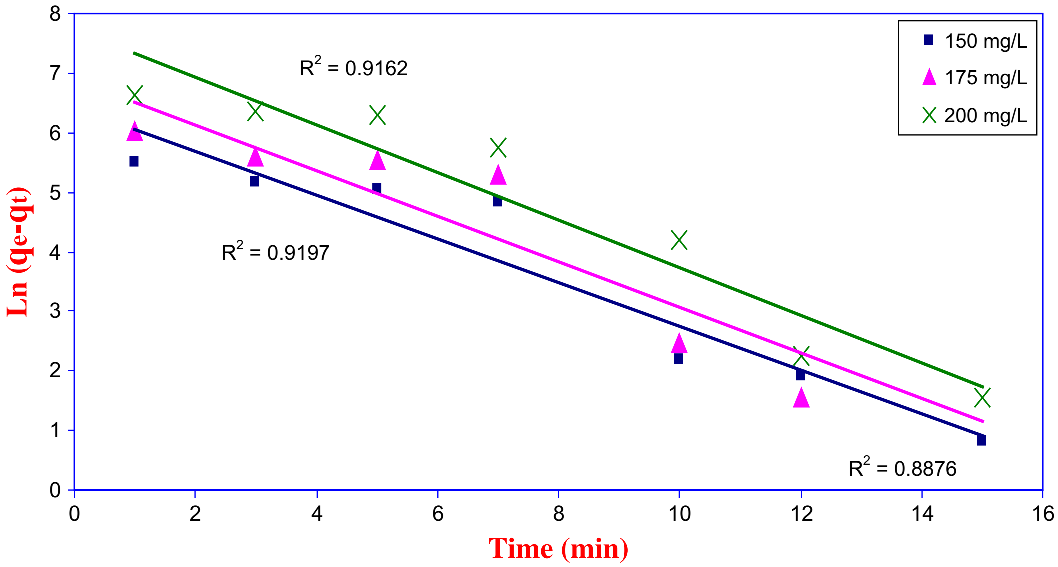


Fig. 11. Pseudo-first-order kinetics of MB dye adsorption on AC-SDeS at different dye concentrations.

Table 5
Kinetic models of adsorption of MB dye at 25ºC

			Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Adsorbent	C_o (mg L^{-1})	q_e (mg g^{-1}) (calc.)	q_e (mg g^{-1}) (exp.)	k_1 (min^{-1})	R^2	q_e (mg g^{-1}) (exp.)	k_2 (g mg^{-1} min^{-1})	R^2
AC-SDeS	150	364.5	82.85	0.366	0.919	369.00	0.0106	1.000
	175	397.25	134.56	0.382	0.887	406.50	0.0062	1.000
	200	433.34	312.31	0.399	0.916	452.48	0.0027	0.990
		Intra-particle diffusion model		Elovich model				
		k_{id} (mg g^{-1} $min^{1/2}$)	R^2	α (mg g^{-1} min)	β (g mg^{-1})	R^2		
	150	10.94	0.902	1.198×10^{10}	0.077	0.906		
	175	17.87	0.893	1.655×10^{8}	0.047	0.905		
	200	34.74	0.908	8.511×10^{4}	0.024	0.904		

coefficients by the first-order-kinetic model were found small values for all examined concentrations. In addition, the estimated q_e values based on the first-order model equation were greatly differed from the experimental values as listed in Table 5. These results indicate that the model is not applicable to describe the adsorption process. Therefore, the adsorption kinetics was further explained by the pseudo-second-order model as given by the following equation [31]:

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

where q_e is the equilibrium adsorption capacity and k_2 is the second-order-rate constant (g mg^{-1} min^{-1}). The values of k_2 at different initial dye concentrations were calculated from the slope and intercept of plot t/q_t vs. t (Fig. 12). The correlation coefficients were found in the range of 0.999–1.000 and the calculated equilibrium adsorption capacity values, $q_{e(calc)}$, were found to correspond to 369.00, 406.50, and 432.48 mg g^{-1} for MB dye concentrations of 150, 175, and 200 mg L^{-1}, respectively. These values are consistent with the experimental data, $q_{e(exp)}$ listed in Table 5 as 364.50, 397.25, and 433.34 mg g^{-1} for the same studied three concentrations of MB dye, respectively. This suggests that the

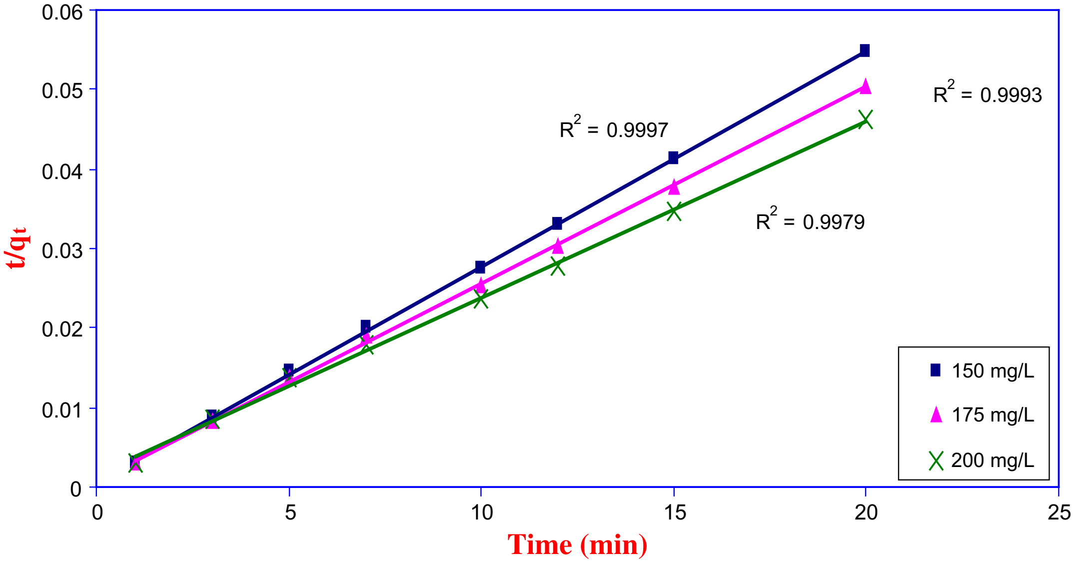


Fig. 12. Pseudo-second-order kinetics of MB dye adsorption on AC-SDeS at different dye concentrations.

adsorptive removal of MB dye by AC-SDeS sorbent is best described by the pseudo-second-order kinetic model.

Weber and Morris plot was also used to investigate the intra-particle diffusion mechanism [31] and the equation used in this respect is given by the following equation:

$$q_t = k_{\mathrm{id}} t^{1/2} + C \quad (11)$$

where C (mg g^{-1}) is the intercept and k_{id} is the intra-particle diffusion rate constant expressed in mg g^{-1} min$^{-1/2}$. The identified values of q_t were found to be linearly correlated with the values of $t^{1/2}$ and the rate constant k_{id} was directly evaluated from the slope of the straight line in Fig. 13. The values of intercept C (Table 5) provide information about the thickness of the boundary layer whereas the resistance to the external mass transfer increases as the intercept increase. The constant C was found to increase with

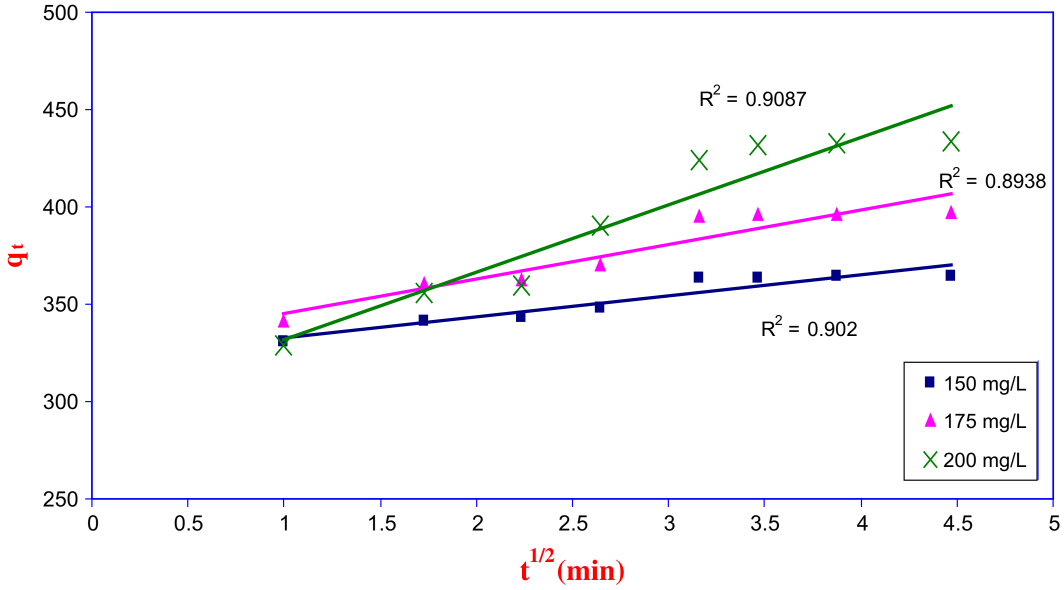


Fig. 13. Intra-particle diffusion plot for the adsorption of MB dye on AC-SDeS at different dye concentrations.

Table 6
Potential applications of AC-SDeS sorbent in removal of MB dye from real water samples

Adsorbent mass	Sample volume	Adjusted pH	Spiked MB dye	Water sample	Removal (%)[a]
AC-SDeS (30.0 mg)	50.0 mL	7.0	125.0 mg L^{-1}	Wastewater	95.90
				Tap water	96.20
				Sea water	ppt

[a] Values are based on triplicate analysis with ±2.0–4.0%.

the increase in the MB dye concentration and this behavior may be attributed to the increase in thickness of the boundary layer. Therefore, the chance of the external mass transfer decreases and hence the chance of internal mass transfer increases.

The R^2 values were found close to the unity as listed in Table 5 and this trend indicates that the suitability of application of this model for the adsorptive removal of MB dye by AC-SDeS sorbent. This may also confirm that the rate-limiting step is the intra-particle diffusion process and the linearity of the plots demonstrate that the intra-particle diffusion process played a significant role in the uptake of MB dye by this sorbent.

The Elovich equation is also used to account for the adsorption of MB dye by AC-SDeS sorbent. This expression is mainly applicable for chemisorptions processes. The equation is often valid for systems in which the adsorbing surface is heterogeneous [32]. The Elovich model is generally expressed by the following equation:

$$q_t = \frac{1}{\beta}\ln \alpha\beta + \frac{1}{\beta}\ln t \qquad (12)$$

where α is the initial adsorption rate (mg g^{-1} min) and β is related to the extent of surface coverage and the activation energy for chemisorption (g mg^{-1}). The plot of q_t vs. ln t gives a linear trace with a slope of $(1/\beta)$ and an intercept of $1/\beta \ln(\alpha\beta)$ with correlation coefficients ($R^2 = 0.906 - 0.904$). The initial adsorption rate, α, was deceased with increasing the initial dye concentration from 150 to 200 mg L^{-1}. The data listed in Table 5 confirm that this model is better in description of the sorption process than the pseudo-first-order model but less efficient than the pseudo-second-order kinetic model.

3.5. Adsorptive decolorization of MB dye from real water samples

The potential application of AC-SDeS sorbent for water treatment of MB dye was also studied and evaluated. Wastewater samples were collected from EL-Mahmoudia canal, Alexandria, tap water and sea water samples were also collected from Alexandria City. These samples were spiked with 125.0 mg L^{-1} of MB dye and extracted using the batch equilibrium technique. The results of this study are listed in Table 6. Good extraction efficiencies for color removal of MB dye from the evaluated samples were obtained. The AC-SDeS sorbent was found to produce 95.90 and 96.20% removal values of MB dye from wastewater and tap water, respectively. However, a precipitate was found upon addition of the MB dye to sea water sample and this behavior may be due to the direct reaction of calcium ion with the dye molecule to form a precipitated complex.

4. Conclusion

In this study, the modified AC-SDeS sorbent was identified as an effective sorbent for removal of MB dye from various water matrices. The studied dye was optimally extracted from aqueous solutions in the pH range of 7.0–13.0 and the equilibrium time was established after 10 min. Two possible mechanisms for MB dye removal were suggested including electrostatic interaction and direct reaction between the sorbent and dye molecule. The collected results proved that Langmuir model yields a better fit for the experimental equilibrium adsorption data than other evaluated models. The kinetic data of adsorptive removal of MB dye by AC-SDeS sorbent are best described by the pseudo-second-order kinetic model and the rate-limiting step is the intra-particle diffusion process. The potential applications of AC-SDeS sorbent for adsorptive removal of MB dye confirmed excellent percentage removal values (95.90–96.20 ± 2.0–4.0%) from real water samples.

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