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Surfactant-coated Tea Waste: Preparation, Characterization and its Application for Methylene Blue Adsorption from Aqueous Solution

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Abstract

This paper reports on the development of organo-modified tea waste (TW) adsorbent prepared by using sodium dodecyl sulfate (SDS) for removing methylene blue (MB), a model cationic dye, from aqueous solution. The natural and modified samples were characterized by scanning electron microscope (SEM), nitrogen physisorption and Fourier transform infrared spectroscopy (FT-IR). Batch adsorption experiments were carried out to remove MB from its aqueous solutions using SDS coated TW (SCTW). Analysis of adsorption results obtained at different temperatures showed that the adsorption pattern on the SCTW can be described perfectly with Langmuir isotherm model compared with Freundlich isotherm model. The adsorption process has been found exothermic in nature and thermodynamic parameters have been calculated. The adsorption kinetic followed the pseudo-second order kinetic model. Desorption studies suggest that MB adsorption onto the SCTW should be mainly controlled by the hydrophobic interaction mechanism, along with a considerable contribution of the cationic exchange mechanism.

Keywords: Tea waste; Sodium dodecylesulfate; Methylene blue; Isotherm; Kinetic; Mechanism

Introduction

Water is a source of life and energy, although millions of people worldwide are suffering with the shortage of fresh and clean drinking water. Rapid pace of industrialization, population expansion, and unplanned urbanization have largely contributed to the severe water pollution and surrounding soils. The main sources of freshwater pollution can be attributed to discharge of untreated sanitary and toxic industrial wastes, dumping of industrial effluent, and runoff from agricultural fields. It is well known that 70–80% of all illnesses in developing countries are related to water contamination, particularly susceptible for women and children. Pollutants discharged in wastewaters can be toxic to aquatic life and cause natural waters to be unfit as potable water sources [1,2].

Dyes are widely used in broad industrial sectors such as textile manufacturing, leather tanning, cosmetics, paper, food processing, and pharmaceutical industries. The annual production of synthetic dyes and dying stuffs are generally exceeding 700,000 tones as reported in the literature [3-5]. In addition, more than 10,000 various types of dyes are available according to the reported color index (CI) by the Society of Dyers and Colorists as well as the American Association of Textile Chemists and Colorists [6]. Generally, more than 100,000 commercial dyes are produced every year for the sake of industrial applications [7]. About 2-50% of the dyestuffs quantity is released into the ecosystem as generated industrial wastewater due to various applications of basic and reactive dyes. However, this subject represents a major environmental problem due to environmental impact on the quality of water [8]. Methylene blue (MB) is the most commonly used substance for dying cotton, wood and silk. It can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. Although MB is seen in some medical uses in large quantities, it can also be widely used in coloring paper, dyeing cottons, wools, coating for paper stocks, etc. Though MB is not strongly hazardous, it can cause some harmful effects. Acute exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice and quadriplegia and tissue necrosis in humans [9].

Treatment of textile effluent nowadays requires an efficient

methodology to face the current challenges. However, several industrial wastewater treatment methodologies and technologies are well known and commonly used for removal and purification of water from organic dyes. These include coagulation, floatation, oxidation, ozonization and nanofiltration as well as biological treatment [3]. On the other hand, adsorption is known as one of the effective methodology for removal of organic and inorganic pollutants and dyes from water matrices [10]. Adsorption technique affords also greater flexibility in the design of the aimed adsorbent for the target pollutant as well as ease and high operational flexibility. In addition, efficiency and superiority of the adsorption technique are mainly relying on the possible harmless of the treated water [11]. Since the performance of an adsorptive separation is directly dependent on the quality and cost-effectiveness of the adsorbent, the last decade has seen continuous improvement in the development of effective adsorbents in the form of activated carbon [12], zeolites [13], clay minerals [14], chitosan [15], lignocelluloses [16], natural minerals [17] and functionalized polymers [18]. However, most of these adsorbents are either not effective (due to diffusion limitation or the lack of active surface sites) or have shown problems like high cost, difficulties of separation from wastewater, or generation of secondary wastes.

The methods to treat dyeing wastewater can be classified in to two types: physical and chemical processes. Among all these methods, adsorption by activated carbon is the most common process for dye removal from wastewater. Although, the process is highly effective, the running costs are high with the need for regeneration after each

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sorption cycle [19]. This has led to the search for other potentially suitable alternative, that is more economical and equally an effective materials for dye removal by adsorption [20]. Recently, comparative studies of cationic and anionic dye adsorption by agricultural solid wastes and some other low-cost adsorbents were reported [3,21-23]. Some of the advantages of using agricultural waste for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selective of adsorption effluent, low cost, free availability and easy regeneration [3]. Besides, the exhausted adsorbents can be disposed of by burning and the heat used for steam generation [24]. However, the application of untreated agricultural or plant waste as adsorbents can also bring several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological oxygen demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the plant wastes [25]. Therefore, the agricultural wastes need to be treated or modified before being used as adsorbent. Tea is consumed by the largest number of people in the world and considered the second most popular beverage in the world. Only water is rated higher in world consumption than tea. It is estimated that somewhere between 18 and 20 billion cups of tea are drunk daily on our planet. Canned or bottled tea drinks as well as instant tea drinks are produced on industrial scale by hot water extraction of tea leaves, and the producers face a problem in disposing of the spent tea leaves after the extraction. Hence, the utilization of such waste is most desirable [26].

Surfactant molecules are composed of both hydrophilic and hydrophobic moieties and extensively used in various industrial processes such as textiles, pulp, and paper industry as well as our daily life. Surfactant-dye associations are important in various dyeing processes such as textiles dyeing, photography, and pharmaceuticals processes [27]. Surfactants play a useful role in the textile dying processes due to their general action as leveling, dispersing and wetting agents. Therefore, surfactants are considered as ideal and suitable components in the textile processing which requires liquid that quickly and uniformly wets the fiber surface. The surfactants act mostly in two ways, either by formation of a complex species with ionic dyes or adsorption into the fiber [28].

In recent years, the use of surfactants in water and wastewater treatment has been specially preferred to separation of metal ions and other toxic substances [8,29-33]. To the best of our knowledge, the application of sodium dodecyl sulfate (SDS) coated tea waste for methylene blue (MB) removal from aqueous environment has not been reported so far. The aim of this study is to present and investigate an efficient methodology to face the current challenges for color treatment of industrial textile wastewater effluent by using a chemically designed and modified adsorbent based on tea waste immobilized anionic surfactant, sodium dodecyl sulfate (SDS), for the adsorptive removal of methylene blue (MB) as an example of cationic dyes. Optimization of all experimental controlling factors and conditions such as reaction contact time, pH, adsorbent dosage, initial dye concentration, mechanism of adsorption as well as temperatures were also explored and evaluated.

Experimental

Materials

The tea waste was collected from Faculty of Fouman Cafeteria. The collected materials were washed several times with boiled water and finally with distilled water to remove any adhering dirt. The washed materials were then dried in the oven at 60°C for 48 h. The dried tea waste

was then ground and sieved into a size range of $100-500 \mu m$. Finally, the resulting product was stored in air- tight container for further use. The methylene blue (MB) purchased from Merck (No.115943) (purity 99.99% and its very low pK_a value (less than 1), was selected as are presentative reactive dye for this study. The MB structure is shown in Scheme 1. A stock solution of MB was prepared by dissolving 1.0 g of MB in 1 L of deionized water, and the concentrations of MB used (50–500 mg/L) were obtained by dilution of the stock solution. The pH of the solution was adjusted to the desired value by adding a small quantity of 0.01 M HCl or 0.01 M NaOH. Sodium dodecyl sulfate (SDS) solutions were prepared from commercially available product (Merck, 8.22050) dissolved in distilled water.

Prepared SDS-coated tea waste (SCTW) and characterization

The solution of SDS was prepared below its critical micellar concentration (CMC = 0.0082 M), as beyond CMC the surface modification was not effective. 100 mL of 2×10^{-3} M SDS solution was treated with 10.0 g often waste and shaken in a temperature controlled shaker at 180 rpm for 3 h at 303 K. The SDS-coated tea waste (SCTW) was then filtered and washed with deionized water till conductance of filtrate was less than 0.05 μ S. The SCTW was then dried in hot air oven at 80°C for 24 h. This was then stored in air tight container for further use.

Fourier transform infrared (FTIR) analysis was applied to determine the surface functional groups, using FTIR spectroscope (FTIR-2000,Bruker), where the spectra were recorded from 4000 to 400 cm⁻¹. Surface morphology was studied using Scanning Electron Microscopy (Vegall-TescanCompany). Specific surface area based on nitrogen physisorption was measured by Sibata surface area apparatus1100. The samples were degassed at 100°C for 2 h prior to the sorption measurement.

Adsorption procedure

Equilibrium isotherms were determined by shaking a fixed mass of SCTW (0.4 g) with 100 mL of MB solutions with different initial concentrations (50,100,200,300,400 and 500 mg/L) in 250 mL glass Erlenmeyer's flasks at a temperature of 20°C and pH =7. The procedure was repeated for temperatures 30, 40 and 50°C. Initial pH adjustments were carried out by adding either a 0.01 M hydrochloric acid or 0.01 M sodium hydroxide solution. After shaking the flasks at 180 rpm for 2 h, small aliquots (2 mL) were withdrawn and centrifuged to remove the adsorbent particles., and then this aliquot was analyzed for the remaining MB concentrations with spectrometry at the wavelength of maximum absorbance, 664 nm using a double beam UV–Vis spectrophotometer (Shimadzu, Model UV2100,Japan).

Kinetic studies

Adsorption kinetics experiments were performed by contacting



200 mL MB solution of different initial concentrations ranging from 50 to 200 mg/L with 0.8 g SCTW in a 500 mL stopper red conical flask at room temperature. At fixed time intervals, the samples were taken from the solution and were analyzed. During the kinetic studies, we controlled the pH value at 7.

Isotherm modeling

The non-linear forms of the Langmuir and Freundlich, isotherm models were used to analyze the equilibrium isotherm data [34]. The fitness of these models was evaluated by the non-linear coefficients of determination (\mathbb{R}^2). The Matlab (version7.3) software package was used for the computing. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful application form any processes of monolayer adsorption. The Langmuir isotherm can be written in the form:

$$q_e = \left(Q_{max} K_L C_e \right) / \left(1 + K_L C_e \right) \tag{1}$$

Where q_e is the adsorbed amount of the dye, C_e is the equilibrium concentration of the dye in solution, Q_{max} is the monolayer adsorption capacity and K_L is Langmuir adsorption constant. The Freundlich isotherm is an empirical equation which assumes that the adsorption occurs on heterogeneous surfaces. The Freundlich equation can be expressed as:

$$q_e = K_F C_e^{1/n} \tag{2}$$

Where
$$K_{F}$$
 and 1/n are fitting constants which can be regarded roughly, the capacity and strength of adsorption, respectively.

Kinetic models

The Lagergren rate equation [35] is one of the most widely used adsorption rate equations for the adsorption of solute from a liquid solution. The pseudo-first-order kinetic model of Lagergren may be represented by:

$$dq / q_e - q = k_1 dt \tag{3}$$

Integrating this equation for the boundary conditions t=0 to t=t and q=0 to $q=q_{,y}$ gives:

$$ln(q_e - q_t) = lnq_e - k_1 t \tag{4}$$

Where \mathbf{q}_{e} and \mathbf{q}_{i} are the amounts of adsorbate (mg/g) at equilibrium and at time t (min), respectively, and \mathbf{k}_{1} is the rate constant of pseudo-first-order adsorption (min^-1). The validity of the model can be checked by linearized plot of $\ln(\mathbf{q}_{e}-\mathbf{q}_{t})$ versus t. Also, the rate constant of pseudo-first-order adsorption is determined from the slope of the plot.

The pseudo-second-order equation based on adsorption equilibrium capacity can be expressed as:

$$dq / \left(q_e - q_t\right)^2 = k_2 dt \tag{5}$$

Taking into account, the boundary conditions t=0 to t=t and q=0 to $q=q_{1}$, the integrated linear form the above equation can be rearranged to follow equation:

$$t/q_{t} = 1/k_{2}q_{e}^{2} + t/q_{e}$$
(6)

Rearranging the variables gives the following equation:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \tag{7}$$

Where the theoretical equilibrium adsorption capacity (q_{e}) and the second-order constants $k_{_2}~(g~mg^{_{-1}}~min^{_{-1}})$ can be determined

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experimentally from the slope and intercept of plot t/q, versus t.

Statistical analysis

All experiments were performed in duplicate and the mean values were presented. The data were analyzed by one-way analysis of variance (ANOVA) using SPSS11.5 for Windows. The data was considered statistically different from control at P<0.05.

Studies on point zero charge (pH_{pzc})

In pH_{pzc} determination, 0.01 M NaCl was prepared and its pH was adjusted in the range of 2–11 by adding 0.01 M NaOH or HCl. Then, 50 mL of 0.01 M NaCl each was put in conical flask and then 0.1 g of the SCTW was added to these solutions. These flasks were kept for 72 h and final pH of the solution was measured by using pH meter. Graphs were then plotted for pH _{final}versus pH _{initial}.

Results and Discussion

FTIR spectral analysis

A closer insight into the biomass surface properties was obtained by comparing the FTIR spectra of prepared samples (Figure 1) in the range of 400–4000 cm⁻¹. FTIR spectra of tea waste (TW), SDS-coated tea waste (SCTW) and SCTW after MB adsorption are shown in Figure 1. In FTIR spectrum of TW (Figure 1a), the broad and intense absorption peaks at around 3400 cm⁻¹ correspond to the O–H stretching vibrations due to inter- and intra-molecular hydrogen bonding of polymeric compounds (macromolecular associations), such as alcohols, phenols and carboxylic acids, as in pectin, cellulose and lignin, thus, showing the presence of "free" hydroxyl groups on the adsorbent surface [36]. The peak at 2919 cm⁻¹ is attributed to the symmetric and asymmetric C–H stretching vibration of aliphatic acids [36]. The precursor had C=O stretching of aldehyde group peaks located on 1709 cm⁻¹ [37]. The peak at 1624 cm⁻¹ is due to asymmetric stretching vibrations of C= Oand the



Figure 1:FTIR spectra of a) TW b) SCTW and c) SCTW after MB adsorption.

peaks observed at 1514 and 1449 cm⁻¹ can be assigned to C=C vibration in aromatic rings. The other prominent peaks are due to NH₂, C=O and -C-C- (1449, 1044 and 827 cm⁻¹, respectively) groups. The assigned peaks at 600–1000 cm⁻¹ may be related to the =C–H of alkenes. It is clear from these peaks that the adsorbent has many functional groups. Most probably, these functional groups are responsible for adsorption via hydrogen bonding with MB. FT-IR spectrum of the SCTW (Figure 1b) shows more intense vibrations compare to TW at 2943, 2917 and 2850 cm⁻¹ assigned to the $-CH_2$ group from SDS and the peak observed at 1236 cm⁻¹ could be assigned to $-SO_3$ stretching vibration., and these suggest that the SDS have been successfully coated the surface of TW. However, the FT-IR spectra of SCTW and SCTW after MB adsorption were found to exhibit similar functional groups due to the domination of the functional groups of TW in this sorbent as the major component in these materials.

Nitrogen physisorption and SEM analysis

The specific surface area of TW and SCTW based on nitrogen physisorption were determined by Brunauer-Emmett-Teller (BET) theory. It was found that the surface area of TW and SCTW were 22 and 45 m²g⁻¹, respectively. As Nadeem et al. reported [38], anionic (SDS) and cationic (CTAB) surfactant enhanced the characteristics of adsorbent better than the nonionic one (Triton X-100). The enhancement can be attributed to the typical properties of micelle formation, adsorption, wetting and solubilization. Being amphipathic in nature, surfactant-modified surfaces can offer enhanced surface area and wetting (water or oil wet) according to the requirement because surfactant molecules are capable of organizing themselves accordingly. Moreover, the presence of electrostatic interactions facilitates the possibility for selective adsorption as well. In mechanism section, we will give details about the role of surfactant in MB adsorption. SEM images of TW, SCTW and SCTW after MB adsorption with two magnifications are presented in Figure 2. It is evident from the obtained SEM images that surfactant modification is significantly responsible to alter the physico-chemical properties of the materials. Figure 2a shows that the TW possesses a rough surface morphology with some pores. The SCTW appear to possess more homogenous surfaces and well organized porous structure than the TW (Figure 2b). The surface of SCTW after MB adsorption(Figure 2c), however, shows that the pores of tea waste are covered with MB molecules.

Effect of initial concentration and contact time on MB adsorption

Figure 3 shows the effect of the initial dye concentration (50–200 mg/L) on the adsorption of MB. It was observed that amount of MB adsorbed was rapid for the first 20 min and there after it proceeded at a slower rate (20-80 min) and finally reached saturation. The equilibrium adsorption increases from 15.54 to 61.50 mg/g, with increase in the initial MB concentration from 50 to 200 mg/L. The findings are because as the initial concentration increases, the mass transfer driving force becomes larger, hence resulting in higher MB adsorption [39]. It is also shown in Figure 3 that the contact time needed for MB solutions with initial concentration provides an important driving force to overcome all mass transfer resistances of the MB between the aqueous and solid phase. However, the experimental data were measured at 120 min to be sure that full equilibrium was attained.

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Point of zero charge $(pH_{_{pzc}})$ studies and the effect of pH on MB adsorption

The point of zero charge $(pH_{_{pzc}})$ is an important factor that determines the linear range of pH sensitivity and then indicates the type of surface active centers and the adsorption ability of the surface [40]. Many researchers studied the point of zero charge of adsorbents that prepared from agricultural solid wastes in order to better understand of adsorption mechanism. Cationicdye adsorption is favored at pH>pH_{pre}, due to presence of functional groups such as OH⁻, COO⁻ groups. Anionic dye adsorption is favored at pH<pH_{pzc} where the surface becomes positively charged [41,42]. The graph of pH_{final} vs pH_{intial} was plotted as shown in Figure 4. The intersections of the curves with the straight line are known as the end points of the pH_{pre}, and this value is 6.3 for SCTW. Figure 5 shows the effect of pH on the adsorption of MB. The experiments were conducted at 50 mL of initial MB concentration, 0.10 g SCTW dose. It was observed that pH gives a significant influence to the adsorption process. MB is cationic dye, which exists in aqueous solution in the form of positively charged ions (MB⁺). As a charged species, the degree of its adsorption onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which inturn is influenced by the solution pH. As shown in Figure 5, the removal percentage was minimum at pH 2 (42%), this increased up to 6 and remained nearly constant (93%) over the initial pH ranges of 6-12. This phenomenon occurred due to the presence of excess H⁺ ions in the adsorbate and the negatively charged surface adsorbent. Lower adsorption of MB at acidic pH (pH<pH_{pre}) is due to the presence of excess H⁺ions competing with the cation groups on the dye for adsorption sites. At higher solution pH (pH>pH_{pzc}), the SCTW possibly negatively charged and enhance the positively charged dye cations through electrostatic forces of attraction. We selected pH=7 for adsorption and kinetic experiments.

Effect of adsorbent dose

Adsorbent dose is an important parameter that strongly influences the adsorption process by affecting the adsorption capacity of the adsorbent [43]. Therefore, the influence of adsorbent dose on MB adsorption by SCTW was investigated in the range of 0.05-0.6 g/100 mL of MB solution (initial concentration: 100 mg/L, pH=7) (Figure 6). The adsorption efficiency increased from 85% to 96% as the adsorbent dose increased from 0.05 to 0.2 g. The increase in the percentage of dye removal with adsorbent dose could be attributed to an increase in the adsorbentsurface area, augmenting the number of adsorption sites available for adsorption, as previously reported [44,45]. The decrease in sorption capacity with increasing dosage of adsorbent at constant dye concentration and volume may be attributed to saturation of adsorption sites due to particulate interaction such asaggregation [46]. Such aggregation would lead to a decrease in total surface area of the adsorbent and an increase in diffusional path length [47]. Therefore, in the following experiments, the adsorbent dose was fixed at 0.2 g/100 mL.

Mechanism of MB adsorption onto SCTW

The surface modification and proposed mechanism of MB adsorption ontoSCTW is shown schematically in Figure 7. In oxides, generally, a monolayer of surfactant molecules (which is called hemimicelles) is formed with the surfactant head group facing toward the oxide surface and its hydrocarbon tail groups into solution. In the event that higher concentrations of the surfactant molecules are presented in the solution, new hydrophobic interactions between hydrocarbons tail-groups will be occurred which results in the

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Figure 3: Effect of contact time and initial concentration (50-200 mg/L) on the adsorption of MB on SCTW (dosage =0.4 g/100 mL and temperature= 298 K).







Figure 6: Effect of adsorbent (SCTW) dosage on adsorption of MB (initial MB concentration: 100 mg/L; solution volume:100 mL, contact time: 120 min; adsorbent dose: 0.05–0.6 (g/100 mL), temperature: 298 K).



formation of discrete surface aggregates termed admicelles. Both of these hemimicelle or admicelle regions formed on the surface of oxides are potential adsorbing locations [48]. Another possible mechanism is the hydrocarbons tail group of surfactant may interact with solid surface through hydrophobic-bonding and the head group directed toward the bulk of the solution, so the surface is potential negative or positive. The mechanism was due to adsorption of SDS onto TW surface (Figure 7). The non-polar portion (alkyl) of SDS may interact with TW surface through hydrophobic-bonding and the polar (negative charged) head group directed toward the bulk of the solution, so the surface is potential negative. So there is negative charge onto surface of SCTW and the mechanism of adsorption about MB onto SCTW may include electrostatic interaction or ion-exchange. Also, some of the MB molecules adsorbed onto the SCTW surface through hydrophobic interaction between MB and hydrocarbon tail of surfactant (Figure 7). We will get more details about it in section 5.10.

Isotherm modeling

Figure 8 and Table 1 show the fitting parameters for the measured isotherm data for MB adsorption onto SCTW in the nonlinear forms of the Langmuir and Freundlich models. By comparing the correlation coefficients R^2 , it can be deduced that the experimental equilibrium adsorption data are well described by the Langmuir equation compared with Freundlich model. This suggests the monolayer coverage of the surface of SCTW by MB molecules. The high adsorption capacity in SCTW could be due to the large amount of surfactant on the surface of

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TW particles, which could result in increasing amounts of negatively charged sites on the surface of TW and finally facilitates the attraction towards the positively dye molecules. Moreover, the Q_{max} decreases with an increase in temperature (from 303 K to 323 K), which specifies an exothermic nature of the existing process. Through the discussion about isotherm constants, it can be predicted whether an adsorption system is favorable or unfavorable. The essential characteristics of the Langmuir isothermcan be expressed by means of R_L , a dimensionless constant referred to as separation factor or equilibrium parameter R_L is defined by:

$$R_{L} = 1/(1+K_{I}C_{0})$$
(8)

Where, C_0 is the highest initial dye concentration (500 mg/L). The parameter suggests the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). As can be seen from Table 1, at all temperatures the R_L values are between 0 and 1.0, indicating that the adsorption of MB onto SCTW is favorable.

The Freundlich equation is suitable for homogeneous and heterogeneous surfaces, indicating a multilayer adsorption [49]. The magnitude of the Freundlich constant gives a measure of favorability of adsorption. Values of n>1 represent a favorable adsorption process [43]. For the present study, the value of n also presents the same trend at all the temperatures indicating the favorable nature of adsorption of MB by SCTW. This is in good agreement with the findings regarding to R_1 values.

Adsorption kinetics studies

The dynamics of the adsorption can be studied by the kinetics of adsorption in terms of the order of the rate constant [50]. The adsorption rate is an important factor for a better choice of material tobe used as an adsorbent; where the adsorbent should have a large adsorption capacity and a fast adsorption rate. Most of adsorption studies used pseudo-first-order and pseudo-second-order models to study the adsorption kinetics. For the pseudo-first-order model, the adsorption rate was expected to be proportional to the first power of concentration, where the adsorption was characterized by diffusion through a boundary. The pseudo-first-order model sometimes does not fit well for the whole range of contact time when it failed theoretically to predict the amount of dye adsorbed and thus deviated from the theory. In that case, the pseudo-second-order equation used was based on the sorption capacity of the solid phase, where the pseudo-secondorder model assumes that chemisorptions may be the rate-controlling step in the adsorption processes [51]. The transient behavior of the MB adsorption process was analyzed by using the pseudo-first and pseudosecond-order kinetic models. Plotting ln(q,,qt) against t permits calculation of k, (Figure 9a). The rate constants, k,, evaluated from these plots with the correlation coefficients obtained are listed in Table 2. Plotting t/q against t (Figure 9b), gives a straight line where k, can be calculated. Usuallythe best-fit model can be selected based on the linear regression correlation coefficient R²values. Generally the kinetic adsorption is better represented by pseudo-second-order model for anionic and cationic dye adsorption. The R² listed (Table 2) for the pseudo-first-order kinetic model was between 0.945 and 0.979. The R² values for pseudo-second-order model were 1, which is higher than the R² values obtained for the pseudo-first-order model. Therefore, the adsorption kinetics could well be satisfactorily more favorably described bypseudo-second-order kinetic model for MB adsorption onto SCTW.

In adsorption process of dye ion on the solid surface, the dye species migrate towards thesurface of the adsorbent. This type of migration proceeds till the concentration of the adsorbate species, adsorbed, on to the surface of the adsorbent. Once equilibrium is attained, the migration of the solute species from the solutions tops. Under this situation, it is possible to measure the magnitude of the distribution of the solute species between the liquid and solid phases. The magnitude of this kind of distribution is a measure of the efficiency of the chosen adsorbent in the adsorbate species. When a powdered solid adsorbent materialis made in contact with a solution containing dyes, the dyes first migrate from the bulk solution to the surface of the liquid film. This surface exerts a diffusion barrier. This barrier may be very significant or less significant [52]. The involvement of a significant quantum of diffusion barrier indicates the dominant role taken up by the film diffusion in the adsorption process. Furthermore, the rate of an adsorption process is controlled either by external diffusion, internal diffusion or by both types of diffusions. The external diffusion controls the migration of the solute species from the solution to theboundary layer of the liquid phase. However, the internal diffusion controls the transfer of the solute species from the external surface of the adsorbent to the internal surface of the pores of the adsorbent material [53]. It is now well established, that during the adsorption of dye over a porous adsorbent, the following three consecutive steps were taken place [54,55]:

(i) Transport of the ingoing adsorbate ions to external surface of the adsorbent (film diffusion).

(ii) Transport of the adsorbate ions within the pores of the adsorbent except for a small amount of adsorption, which occurs on the external surface (particle diffusion).

(iii) Adsorption of the ingoing adsorbate ions on the interior surface of the adsorbent.

Out of these three processes, the third process is considered to be very fast and is not the rate limiting step in the uptake of organic compounds. The remaining two steps impart the following three possibilities:

Case 1 External transport>internal transport, where rate is governed by particle diffusion.

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[1				
	Langmuir				
Temperature (K)	293	303	313	323	
Q _{max} (mg/g)	158.18	256.74	184.05	146.94	
K _L (L/mg)	0.0357	0.0175	0.0261	0.05	
RL	0.05305	0.10256	0.07117	0.03846	
^R 2	0.9882	0.9945	0.9927	0.9907	
	Freundlich				
Temperature (K)	293	303	313	323	
n	1.72	1.36	1.59	1.94	
k _F (mg/g)(dm³/mg) ^{1/n}	10.45	7.08	8.96	13.96	
^R 2	0.9354	0.9732	0.9710	0.9229	

Table 1: Isotherm parameters for MB adsorption onto SCTW.

C ₀ (mg/L)	pseudo-first order			pseudo-second order		
	q _e (mg/g)	k ₁ (1/min)	R ²	q _e (mg/g)	k ₂ (g/mg.min)	R ²
50	0.056	0.0077	0.9569	15.53	0.1908	0.9999
100	0.251	0.0129	0.9793	31.06	0.4149	0.9999
200	0.796	0.023	0.9452	61.35	0.0010	0.9999

Table 2: Kinetic parameters for the adsorption of MB onto SCTW based on Lagergren rate equation.

S

Case 2 External transport<internal transport, where the rate is governed by film diffusion.

Case 3 External transport \approx internal transport, which accounts for the transport of the adsorbate ions to the boundary and may not be possible with in a significant rate, which later on gives rise to the formation of a liquid film surrounded by the adsorbent particles with a proper concentration gradient. In order to predict the actual slow step involved in the adsorption process, the kinetic data were further analyzed using the Boyd model given by Eq. (8) [56]

$$B_t = -0.4977 - ln(1-F) \tag{8}$$

F represents the fraction of solute adsorbed at anytime, t (h), as calculated using Eq. (9)

$$F = q_t / q_e \tag{9}$$

Where q_t and q_e are amounts adsorbed after time t and after infinite time (160 min), respectively. The calculated B_t values were plotted against time t(h), as shown in Figure 10. The plot of B_t vs time distinguishes between the film-diffusion and particle-diffusioncontrolled rates of adsorption. The linear lines for all MB initial concentrations did no pass through the origin and the points were scattered. This indicated that the adsorption of MB on the SCTW was mainly governed by external mass transport where particle diffusion was the ratelimiting step [56].

Adsorption thermodynamics

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously [57]. Gibb's free energy change, ΔG° , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative value. The thermodynamic parameters of ΔG° , enthalpy change, ΔH° , and entropy change, ΔS° , for the adsorption processes are calculated using the following equations [57,58].

$$\Delta G^{\circ} = -RT \ln K_{\rm p} \tag{10}$$

 $K_{\rm D}$, is given by the following equation:

$$K_D = q_e / C_e \tag{11}$$

Where K_{D} is the distribution coefficient and:

$$* = (1 - \theta) e^{-(E/RT)}$$
 (12)

Where, R is universal gas constant (8.314 J/mol K) and T is the absolute temperature in K. A plot of lnK_D versus 1/T was found to be linear. The values of ΔH° and ΔS° were respectively determined from the slope and intercept of the plot. The thermodynamic parameter, $\Delta G^{\circ}\!\!\!$, is shown in Table 3. ΔH° and ΔS° for the sorption process were calculated to be -0.05 kJ/mol and +3.20 J/mol K, respectively. The negative value of ΔG° confirms the feasibility of the process and the spontaneous nature of sorption with a high preference for MB to adsorb onto SCTW. The value of ΔH° was negative, indicating that the sorption reaction is exothermic. These values did not indicate strong chemisorptive bond formation between the dye molecules and the adsorbent surface. The positive value of ΔS^0 (Table 3) shows that the freedom of MB is not too restricted in SCTW confirming a physical adsorption, which is further confirmed by the relatively low values of ΔG^0 . Also, the positive ΔS° value reveals increased randomness at the interface of solid and liquid, indicating the accumulation of MB.

The activation energy (E_a) was obtained from the slope of plot ln (1- θ)against 1/T, where the surface coverage (θ) was calculated from the relation eqs. (13) [58,59]:

$$\theta = 1 - (C/C_0) \tag{13}$$

Where: C_0 and C are the initial and residual concentration of MB in solution, respectively (mg/L).

In order to further support the assertion that physical adsorption is the predominant mechanism, the values of sticking probability (S^*) was estimated from the experimental data. It was calculated using a modified Arrhenius type equation related to surface coverage as expressed in Equation (14) [58,60].

$$S^* = (1-\theta) e^{-(E/RT)}$$
(14)

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Langmuir isotherm						
Temperature (K)	∆G° (kJ/mol)	∆Hº (kJ/mol)	∆S° (J/mol K)	E _a (kJ/mol)	S*	
293	-1.644					
313	-1.637	-0.62	+3.20	-0.05	0.117	
323	-1.555					

Table 3: Thermodynamic parameters for the adsorption of MB onto SCTW.



Figure 9: Kinetic models for adsorption of MB onto SCTW.(a) pseudo-firstorder and (b) pseudo-second-order rate equations.



The parameter S^* indicates the measure of the potential of an adsorbate to remain on the adsorbent indefinitely. It can be expressed as in Table 3. The effect of temperature on the sticking probability was evaluated throughout the temperature range from 293 to 323 K by calculating the surface coverage at the various temperatures. The apparent activation energy (E_a) and the sticking probability (S^*) are estimated from the plot with reasonable good fit for the MB on the SCTW. The E_a values calculated from the slope of the plot were found to be -0.05 kJ/mol. The negative values of E_a indicate that lower solution temperatures favors MB removal by adsorption onto SCTW and the adsorption process is exothermic in nature. Relatively low values of E_a suggest that MB adsorption is a diffusion controlled process. The results as shown in Table 3 indicate that the probability of MB sticking to the SCTWsurface is very high as $0 < S^* < 1$ for MB (Table 3). These values confirm that, the sorption process is physisorption[60].

Desorption studies of MB

Desorption studies can help enlightening the mechanism of an adsorption process. If the dye adsorbed onto the adsorbent can be desorbed by water, it can be said that the attachment of the dye onto the adsorbent is by weak bonds. If the strong bases, such as NaOH can desorbs the dye, it can be said that the attachment of the dye onto the adsorbent is by ion exchange [61]. Hence, neutral distilled water was used in the elution of MB molecules from the SCTW followed by NaOH solution. The percentage of desorption obtained were 17% and 20% for using neutral distilled water and 0.1 N NaOH solution, respectively. The fact that the low desorption occurred with distilled water and NaOH solution suggests that adsorption of MB onto SCTW carries out significantly by another mechanism. The mode of existence of surfactant molecules on solid surface has been investigated widely [48]. As we mentioned in section 5.6, a possible mechanism is the hydrocarbons tail group of surfactant may interact with solid surface through hydrophobic-bonding and the head group directed toward the bulk of the solution, so the surface is potential negative or positive. Consequently, it can be conceived from the result of desorption by NaOH that some surfactant molecular arrange in this manner in the research. Here, the above conclusion related to ionexchange mechanism is clearly confirms. Taking all the results that have been discussed above into account, it is proposed that enhanced hydrophobic interaction is the predominant mechanism contributing to the increased MB adsorption on the SCTW, followed by a certain amount of the cationic exchange. For better illustration of the process of adsorption, a suggested adsorption structure was shown in Figure 7.

Cost evaluation of the adsorbent

Adsorbent cost is important to practicability. Cost of the adsorbent prepared in this work is mainly from use of surfactant. The market price of SDS is about US \$7000 per metric ton. The cost of the prepared adsorbent is around US \$630 per metric ton according to the ratio of TW to the surfactant (10:1). The market price of commercial activated carbon is about US \$500–800 per metric ton. It is clear that the cost of the two adsorbent is similar. Compared with activated carbon, however, SDS modified TW adsorbent has some advantages, such as

simple preparation procedure and low energy consumption, and has good application prospect.

Conclusions

The results of this investigation show that sodium dodecyle sulfate coated tea waste (SCTW) has excellent adsorption capacity for the removal of methylene blue from aqueous solutions. SEM shows that morphological feature of TW changed after modification. FTIR results suggest that the SDS have been successfully coated the surface of TW. The adsorption isotherm experiment was conducted at different temperatures (293,303,313 and 323 K), and it was found that the uptake of MB decreased with increasing temperature and hence adsorption process is exothermic in nature. The equilibrium data were analyzed by the Langmuir and Freundlich models and the Langmuir model was found to fit the equilibrium data better. The adsorption capacity was found to be 256 mgg⁻¹ at 303 K. The pseudo-second order kinetic model agrees very well with the dynamic behavior for the adsorption of MB onto surfactant modified tea waste. In addition, various thermodynamic parameters such as changes in enthalpy, entropy, and the Gibbs free energy were calculated, showing adsorption to be an exothermic process. The desorption studies implied that the hydrophobic interaction and cationic exchange models controlled simultaneously during the adsorption process, but the former is a dominant mechanism. The developed SCTW not only has demonstrated higher adsorption efficiency and fast kinetics but also have shown additional benefits like cost-effectiveness and environmental-friendliness. It can be concluded to be a promising advanced adsorbent in environmental pollution cleanup.

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