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Selective separation of Light green and Safranin O from aqueous solution using *Salvadora persica* (Miswak) powder as a new biosorbent



Elhossein A. Moawed ^{a,*}, Abdullah B. Abulkibash ^b

^a Chemistry Department, Faculty of Science, Damietta University, Damietta, Egypt

^b Chemistry Department, King Fahd University of Petroleum & Mineral, Dhahran, Saudi Arabia

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Abstract In this paper a novel solid phase extraction method to remove Light green (acid dye) and Safranin O (basic dye) using *Salvadora persica* (Miswak) powder as a new biosorbent is described. The adsorption conditions such as contact time, initial dye concentration, pH and temperature were studied by using batch system. After optimization, Miswak showed an excellent removal rate for dyes, the extraction of the dyes was accomplished in a period range of 1–10 min. The adsorption kinetics data were in good agreement with the pseudo-second-order rate model ($R^2 = 0.98$) and the initial sorption rate (h) was found to be $0.01 \text{ g mmol}^{-1} \text{ min}^{-1}$. The new adsorbent was found to have a maximum adsorption capacity of 17.3 mmol/g . The adsorption isotherms could be adequately described by the Freundlich equation ($R^2 = 0.91$) and the $1/n$ value is 0.9, which attributed to the heterogeneous surface structure of the Miswak. Study of the variation of the sorption of the tested dyes with temperature yielded values for ΔH , ΔS , and ΔG of -21.0 , $-0.056.3$ and -4.2 kJ mol^{-1} , respectively.

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1. Introduction

Light green is the standard dye for staining collagen in contrast to acid fuchsine in Masson's trichrome. It is a component of

Papanicolaou's EA series in conjunction with eosin Y and bis-marck brown. It is also used extensively in plant histology. Safranin O is a biological stain used in histology and cytology. It is commonly used for staining gram negative bacteria red in smears to contrast with the blue gram positive organisms. It can also be used for the detection of cartilage, mucin and mast cell granules. Dye residues are esthetically unpleasant and interfere with the transmission of light necessary to photosynthesis, causing disturbance in the ecological systems of the receiving water. Several techniques such as coagulation, photodegradation and ozonation are available for the treatment of industrial wastewaters (Bhatnagar and Sillanpaa, 2010; Gozmen et al., 2009; Ramakrishnan and Nagarajan, 2009). These methods are expensive, produce concentrated sludges

* Corresponding author. Current address: Department of Chemistry, Faculty of Education, Dammam University, P.O. Box 2375, Saudi Arabia. Tel.: +966 050 524 1921.

E-mail address: eamoawed@yahoo.com (E.A. Moawed).

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or are inadequate to treat large volumes of effluent without the risk of clogging. Research is therefore needed to develop new alternative environmental friendly applications (Brito et al., 2010). The adsorption processes give the best results as they can be used to remove different types of coloring materials, providing an attractive treatment, especially if “low cost” adsorbents are available. A variety of agricultural biomass has been used for biosorption process, namely peat (Allen et al., 2004), pinus bark powder (Ahmad, 2009), tomato plant root and green carbon (Kannan et al., 2009) also, deoiled soya (Mittal et al., 2010), alligator weed, japonica, rice bran, wheat bran (Wang et al., 2008), skin almond waste (Atmani et al., 2009), palm kernel fiber (El-Sayed, 2011), barley husk (Robinson et al., 2002), lemon peel (Kumar, 2007) and pumpkin seed hull (Hameed and El-Khaiary, 2008). However, new, economical, locally available and highly effective dye biosorbents are still needed to investigate for the scavenging of dye from wastewater.

Salvadora persica (Arak, Galenia asiatica, Meswak, Miswak, Peelu, Pilu, *Salvadora indica*, toothbrush tree and Mustard tree), is a species of *Salvadora*. Used for centuries as a natural toothbrush, it has been promoted by the World Health Organization for oral hygiene use. Research suggests that it contains a number of medically beneficial properties including abrasives, antiseptics, astringent, detergents, enzyme inhibitors, and fluoride (Amoian et al., 2010; Darmani et al., 2003; Sofrata, 2010). *Salvadora persica* is a small tree or shrub with a crooked trunk, seldom more than one foot in diameter. The root bark of the tree is similar to sand, and the inner surfaces are an even lighter shade of brown (Ramoliya et al., 2004; Reddy et al., 2008). *Salvadora persica* is a popular chewing stick throughout the Indian subcontinent, as well as the wider Muslim world. In addition, commonly referred to as Miswak, many Muslims consider chewing *Salvadora persica* to be a practice recommended by the Islamic prophet Muhammad. The infrared and atomic emission spectroscopic techniques were used in the study of the organic and inorganic structures and composition of *Salvadora* sticks. The results showed that the organic part of the sticks of *Salvadora persica* consists mainly of cellulose, hemicelluloses and lignin. The lignin content in the pulp is higher than its content in the outer layers (Bahabri, 2000). The inorganic part provides strong evidence that the mineralogy of this content depends on the geography of the sample's regions (Bahabri, 2000).

In this study, *Salvadora persica* as a novel sorbent had been used for removal of acidic and basic dyes. The Miswak properties were characterized by elemental analysis (EA), Fourier transform infrared analysis (FT-IR) and thermogravimetric analysis (TGA). The sorption behavior of Light green and Safranin O onto the Miswak has been studied to optimize the conditions for the best preconcentration and removal of dyes. The data have been obtained for kinetic, thermodynamic, and equilibrium situations.

2. Experimental

2.1. Materials

Salvadora persica sticks (Miswak) were obtained from a plantation in El-Khtrichia, El-Qtif, Saudi Arabia. The sticks were washed by tap and distilled water to remove impurities such

Table 1 Physical and chemical characterization of *Salvadora persica* (Miswak) powder.

Property	
<i>IR spectra</i>	
ν -OH and -NH ₂ (cm ⁻¹)	A broad band between 3600–3000
ν -CH aliphatic (cm ⁻¹)	2926.8
ν C=O, C=C and -NH (cm ⁻¹)	1676.3, 1624.7 and 1524.7, respectively
ν C-O-C (cm ⁻¹)	1016.2
<i>¹H NMR spectra</i>	
Aliphatic -CH ₂ , -CH ₃ (ppm)	1.25 and 1.86
Alcoholic and phenolic -OH (ppm)	2.58 and 4.50
Aryl protons Ar-H (ppm)	7.28
<i>¹³C spectra</i>	
(ppm)	76.74, 77.00 and 77.26
<i>Elemental analysis</i>	
C, H, N and S (%)	33.2, 5.0, 2.6 and 4.8
Color	Brown
Bulk density (g/cm ³)	0.54
pH (1% solution)	6.3
pH _{ZPC}	5.2
Conductivity (1%) (mS/cm)	2.83
Iodine number (mmol g ⁻¹)	0.84
Total acidity (mmol g ⁻¹)	5.38
Phenolic (mmol g ⁻¹)	3.28
Carboxylic acid (mmol g ⁻¹)	1.55
Lactones (mmol g ⁻¹)	0.55

as sand. The washed sticks were dried in an oven at 105 °C for 24 h and blended in a food-processing blender. The dried Miswak powder was sieved from < 45 to > 250 μm size. The particles between 90 and 250 μm were used for adsorption studies. The characteristics of the Miswak powder have been reported in Table 1.

A 1 mg mL⁻¹ stock solution of Light green (C₃₇H₃₇N₂O₉S₃, 749.9 g/mol, C.I. number: 42095, Fig. 1) and Safranin O (C₂₀H₁₉N₄Cl, 350.8 g/mol, C.I. number: 50240, Fig. 1) was prepared by dissolving 0.1 g of pure dye in 5 mL of water and diluting the solution to 100 mL.

2.2. Apparatus

All spectrophotometric measurements were performed on a Shimadzu Model UV-1800 (Shimadzu Corporation, Japan). FT-IR spectra were obtained using Shimadzu, model FTIR-8400. Morphological features of samples were obtained with a JEOL JEM-1200 EX II Electron Microscope. The pH meter (Jeneway, model 3510) was used in the pH measurements. The heavy metal contents were determined by using Inductive Coupled Plasma/Optical Emission Spectrometry (ICP/OES) model Vista PRO obtained from the Varian Company.

2.3. Recommended procedures

Adsorption experiments were carried out by agitating 0.1 g of Miswak with 50 ml of dye solution of desired concentration. Light green and Safranin O concentration was estimated spectrophotometrically by monitoring the absorbance at 521

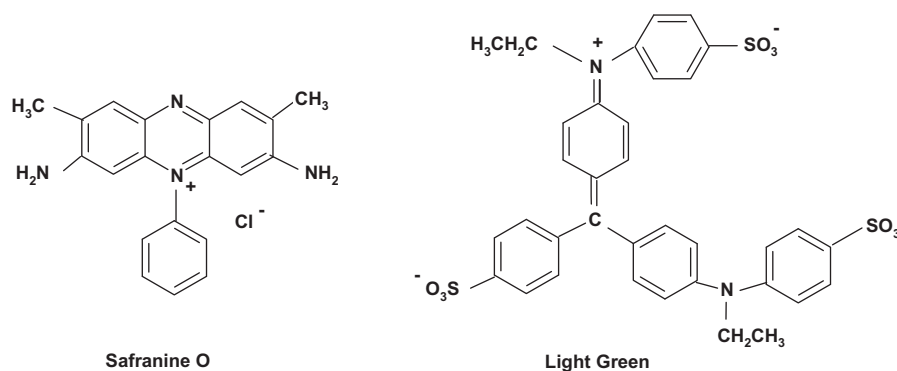


Figure 1 Structure of Light green and Safranin O dyes.

and 632 nm using UV-Vis spectrophotometer. The dye solution was separated from the adsorbent by centrifugation at 2000 rpm for 15 min and its absorbance was measured (Ofomaja and Naidoo, 2010). The sorption percentage of dyes was calculated ($\%E = [(C_o - C)/C_o] \times 100$) where C_o and C are the initial and final concentrations of dyes in solution, respectively.

2.3.1. Effect of pH

A 25 mL portion of dye solutions ($5 \mu\text{g mL}^{-1}$) of Light green and Safranin O from single dye solutions was shaken with 0.1 g of Miswak for 30 min. The pH of the dye solution was adjusted before equilibration with HCl or NaOH over a range of 1–14. After the equilibration, the remaining dye was determined by the recommended method.

2.3.2. Effect of time

The effect of shaking time on the extraction efficiency of dye was studied. For that purpose, 0.1 g of Miswak was added to 25 mL of sample at the optimum pH and automatic shaking for different time intervals (1–60 min).

2.3.3. Equilibrium studies

The effect of dye concentration on the sorption of dye onto Miswak was examined. Different concentrations of dye (0.1 – 1 mg mL^{-1}) were equilibrated with 0.05 g of Miswak, which was automatically shaken for 30 min at room temperature. After equilibration, the remaining dye in the solution was determined.

2.3.4. Effect of temperature

The effect of temperature on the sorption of Light green and Safranin O onto Miswak was studied. 0.1 g of Miswak was added to 25 mL of sample at the optimum pH and shaking for 30 min at different temperatures (25 – 70°C). After the equilibration, the remaining dye was determined by the recommended method.

3. Results and discussion

3.1. Characteristics of Miswak

The elemental analysis of Miswak sample was studied. The result shows that the percentage composition of Miswak is given

as carbon 33.17%, hydrogen 4.99%, nitrogen 2.64%, sulfur 4.80% and 54.40% for oxygen and metal ions.

The infrared spectrum of Miswak was tested using KBr technique. FT-IR measurement for the Miswak showed the presence of the following groups: $-\text{OH}$ and $-\text{NH}_2$ (A broad absorption between 3600 – 3000 cm^{-1}), $-\text{CH}$ aliphatic (2926.8 cm^{-1}), $\text{C}=\text{O}$ (1676.3 cm^{-1}), $\text{C}=\text{C}$ aromatic (1624.7 cm^{-1}), $-\text{NH}$ (1524.7 cm^{-1}) and $\text{C}-\text{O}-\text{C}$ (1016.2 cm^{-1}) (Table 1).

^1H NMR spectra for the Miswak are listed in Table 1. In the spectra, two characteristic peaks were observed at 1.25 ppm and 1.86 ppm standing for the chemical shifts of H in aliphatic $-\text{CH}$. In addition, two single peaks attached were observed at 2.58 ppm and 4.50 ppm due to aliphatic $-\text{OH}$ and phenolic $-\text{OH}$, respectively. While, single peak in the region 7.28 ppm was appeared which implies the H of target compound belongs to aryl protons (Ar-H).

The total surface acid sites of Miswak matching the carboxylic, phenolic and lactonic sites were determined using a 0.01 mol L^{-1} NaOH solution. The carboxylic and lactonic sites were titrated with a 0.01 mol L^{-1} Na_2CO_3 solution and the carboxylic sites were determined with a 0.01 mol L^{-1} NaHCO_3 solution, and the phenolic sites were estimated by difference. The Miswak was shown to contain 0.55 mmol g^{-1} of lactonic group, 1.55 mmol g^{-1} of carboxylic group, 3.28 mmol g^{-1} of phenolic group and a total acidity of 5.38 mmol g^{-1} . The amount of surface basic site was determined by using 0.01 mol L^{-1} HCl. The total basicity estimated is 0.42 mmol g^{-1} (Table 1). By comparing the total acidic sites of Miswak material with basic sites, the total acidic sites are higher than the number of basic sites ($5.38 \text{ mmol g}^{-1} : 0.42 \text{ mmol g}^{-1} \approx 13:1$). These results indicate that the surface of Miswak is mostly acidic and good adsorbent for removal of basic dyes. In addition, we suggest the use of *Salvadora persica* sticks in medicine as toothpaste because they contain chemical substances that have acidic characters, which inhibit plaque formation.

The pH of Miswak suspension was measured to investigate the change in pH due to any soluble species from the natural material in water. The sample (1% W/V) was shaken in distilled water for 3 h and then the pH was measured. The pH obtained was 6.3. These results indicate mainly that the material of Miswak has an acidic effect and it is in good agreement with the results obtained in the previous section.

pH_{ZPC} is the pH when the charge on the Miswak surface is zero (zero point charge). The pH_{ZPC} value was determined to be approximately 5.2 for the Miswak. At pH lower than the pH_{ZPC} ($pH < 5.2$), the surface of the Miswak is positively charged while at pH greater than pH_{ZPC} , the surface of the Miswak becomes negatively charged.

The results from the elemental analysis, FT-IR, 1H NMR and surface sites sections showed that the organic part of the sticks of *Salvadora persica* consists mainly of cellulose, hemicelluloses and lignin. In addition, the main functional groups were in the order phenolic, carboxylic, alcoholic and amine groups, respectively.

The metal contents were determined by digestion of the Miswak sample by using conc. nitric acid and then dissolving by distilled water. The results show that the Miswak contains: K:235.3 mg g^{-1} ; Na:177.1 mg g^{-1} ; Al:0.37 mg g^{-1} ; Fe:0.36 mg g^{-1} ; Cu:0.08 mg g^{-1} ; Zn:0.04 mg g^{-1} ; Mn:0.02 mg g^{-1} ; Cr:7.8 μg^{-1} and Ni:6.7 μg^{-1} (certified by WQC lab of Greater Cairo Water Company). The metal provides strong evidence that the mineralogy of this content depends on the geography of the sample's regions. This result shows that the mineral contents of *Salvadora persica* were participating in ion-exchange process during removal of pollutant.

Bulk density of Miswak measurement was carried out in a 25 mL density bottle. The Miswak powder was added to the density bottle with gentle tapping to ensure that the particles settle to the bottom and all air spaces are filled. The mass of the density bottle containing the Miswak powder was then determined. Bulk density = Mass of Miswak/25 cm^3 . The density of the Miswak obtained was 0.54 g/cm^3 .

The surface morphology of Miswak powder was investigated by scanning electron microscope (SEM) at a magnification of 1500. The SEM images of Miswak are shown in Fig. 2. The microstructure of Miswak image showed that the surface could be seen to contain amounts of pores; average pore size is equal to 12.56 μm , indicating that this material presents good characteristics to be employed as a natural adsorbent for dye uptake. It is believed that these pores provide a ready access and large surface area for the sorption of dyes on the binding sites.

To determine the adsorption capacity (iodine number), 25 ml of iodine solution of 0.05 mol/L was added to three flasks, which contained 0.25 g of Miswak. The flasks were then

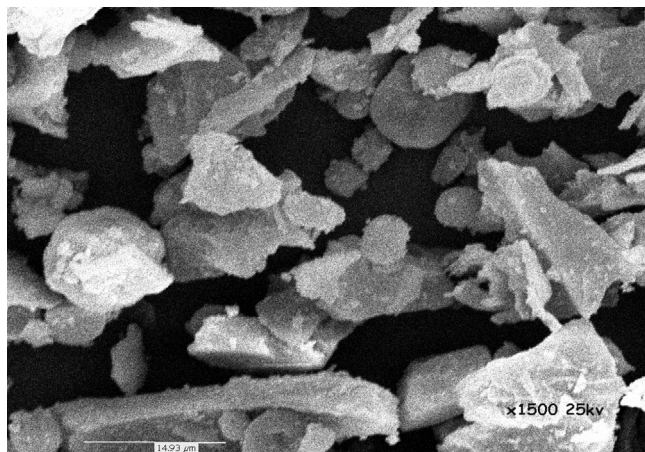


Figure 2 SEM image of Miswak powder.

shaken for 24 h to ensure equilibrium adsorption of iodine onto Miswak. The iodine number (mmol/g) was determined from the titration of the residual solution of 10 ml with 0.05 mol/L sodium thiosulfate in the presence of 1 ml of 1 wt.% starch solution as an indicator. The iodine adsorption capacity was determined from the adsorbed iodine/unit mass of the adsorbent at the residual iodine concentration. The sorption capacity of Miswak for iodine was estimated to be 0.84 mmol/g (106.6 mg/g). The iodine number of Miswak is compared with other biosorbents (Namasivayam et al., 2007; Ofomaja and Naidoo, 2010; Ofomaja and Unuabonah, 2011); the Miswak exhibits better capacity values in comparison to biosorbents.

Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions on their total concentration, mobility, and valence. The value of electrical conductivity was 2.83 mS/cm for 1% Miswak solution. The results obtained showed higher values of conductivity of the Miswak solution than activated carbon (Kavitha and Namasivayam, 2007; Kavitha and Namasivayam, 2008; Namasivayam and Sangeetha, 2005) that could be attributed to a high content of dissolved ions and polar compounds.

3.2. Sorption behavior of Light green and Safranin O dyes

3.2.1. Effect of sample pH

Effect of sample pH on the sorption behavior of Light green and Safranin O dyes was studied in the pH range of 1–13 using 25 mL of dye solution. The samples were processed according to the recommended batch experiment. As can be seen in Fig. 3, maximum sorption of dye by Miswak occurred at a pH range of 1–3 and 11–13 for Light green and Safranin O, respectively. The sorption percentage sequence was in the order Safranin O > Light green in alkaline medium while the sorption percentage of Light green > Safranin O in acidic medium, depends on the charge of the dye molecule. At pH lower than the pH_{ZPC} ($pH < 5.2$), the surface of the Miswak is positively charged while at pH greater than pH_{ZPC} , the surface of the Miswak becomes negatively charged. Therefore the basic molecules (Safranin O) adsorbed due to electrostatic

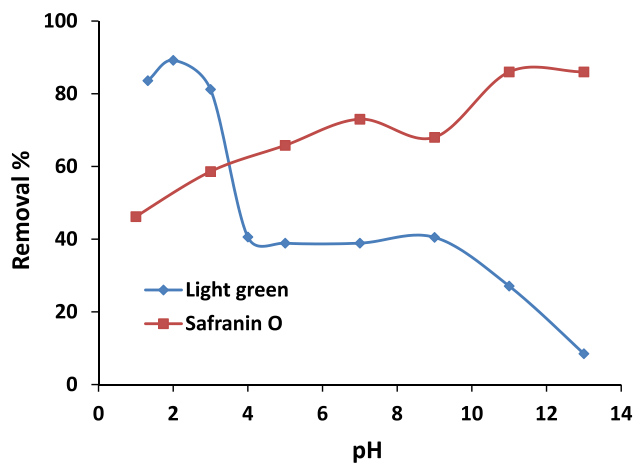


Figure 3 Effect of initial pH on the adsorption of Light green and Safranin O by Miswak.

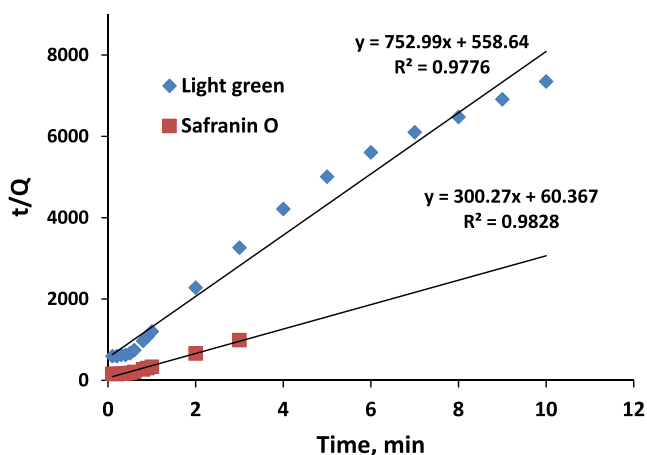


Figure 4 Pseudo-second-order plot for the adsorption of Light green and Safranin O by Miswak.

interaction of dyes with the negatively charged surface of the Miswak in alkaline medium could reasonably suggest that the sorption of Safranin O onto Miswak may proceed via ion association mechanism. The sorption percentage of Light green decreases with the increase of the pH values indicating the repulsion between the negative sites of Miswak and sulfonic groups of Light green molecules in alkaline medium while the sorption of Light green increases in acidic medium due to the adsorption neutral molecule of Light green onto Miswak. Therefore, the possible mechanism that has been proposed for the sorption of Light green onto Miswak is solvent extraction. The obtained results confirm that the sorption mechanism depends on the charged sites of Miswak and pH values. Finally, the soluble polar compounds react with dye molecules and then get adsorbed as neutral molecules onto Miswak particle. This fact is the reason for the Miswak to have a higher capacity sorbent.

The values of the separation factor (α) for the tested dyes were calculated ($\alpha = E_1/E_2$), where E_1 and E_2 are the uptake of dye onto Miswak. The results obtained show that the selectivity sequence is in the order Safranin O > Light green at the pH 13 ($\alpha_{S,O/L,G} = 10.12$) while the value of $\alpha_{L,G/S,O}$ is 1.8 at pH 1. These results show that controlling the pH can play a role in enhancing the selectivity of the dye separation with Miswak.

3.2.2. Sorption kinetics

The influence of shaking time on the percentage of sorption is recognized of significant importance to determine the possible discrimination order of Miswak behavior toward acid and base dyes. The sorption of Light green and Safranin O by Miswak

was found to be rapid and reached equilibrium within about 15.0 min and 1.0 min shaking time, respectively. It is evident from the results obtained that the equilibrium between Safranin O and the Miswak is faster than Light green. This rapid extraction is due to the application of Miswak by using batch technique, which is relatively fast and efficient of the Miswak sorbent as compared to the other biosorbents (Baccar et al., 2010; Kumar and Ahmad, 2011; Saeed et al., 2010).

The Morris-Weber [$Q_t = k_i \sqrt{t}$] model was applied to explain the diffusion mechanism of Light green and Safranin O onto Miswak where k_i is the intraparticle diffusion rate constant ($\text{mmol g}^{-1} \text{min}^{-1/2}$). The sorbed dye concentration (Q_t) at time t was plotted against the square root of time. From the results, we observed that the plot of Q_t versus $t^{1/2}$ is a two-stage line that does not pass through the origin with good determination coefficient ($R^2 = 0.956$). The average values of k_i of first stage ($3.32 \text{ mmol g}^{-1} \text{min}^{-1/2}$) are higher than the value of k_i second stage ($0.15 \text{ mmol g}^{-1} \text{min}^{-1/2}$).

The pseudo first order [$\log(Q_e - Q_t) = (\log Q_e) - (k_1 t / 2.303)$] and pseudo second order [$t/Q_t = (1/k_2 Q_e^2) + (t/Q_e)$] kinetic models are tested to fit the experimental data for the sorption of Light green and Safranin O onto Miswak (Fig. 4). The determination coefficient (R^2) values for pseudo second order sorption model (0.980) are higher than R^2 values for pseudo first order kinetic (0.912). Also, the chi-square model ($\chi^2 = \sum (Q_e - Q_e)^2 / Q_e$) was used for comparing the experimental sorption capacity against those obtained from the predicted pseudo first order and pseudo second order equations. Where Q_e is the capacity by calculating from the model and Q_c is the experimental data of the capacity. From Table 2 it was seen that the values of χ^2 (0.02 and 0.03) obtained from pseudo second order model are less than those obtained by using pseudo first order model ($\chi^2 = 0.32$ and 0.35). This suggests that the pseudo second order adsorption mechanism is predominant. The initial sorption rate (h) can be defined as [$h = k_2 Q_e^2$]. The values of h were calculated from the intercept and it is found to be 0.002 and 0.017 $\text{g mmol}^{-1} \text{min}^{-1}$ for Safranin O and Light green, respectively, which showed that the rate of sorption is dependent on the size of the dye (Table 2).

3.2.3. Sorption isotherms

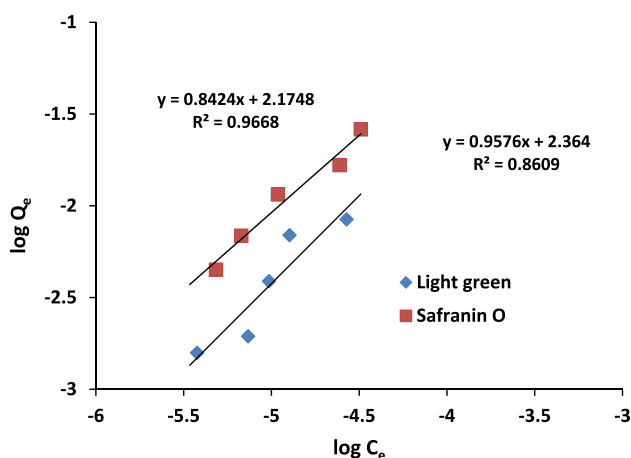
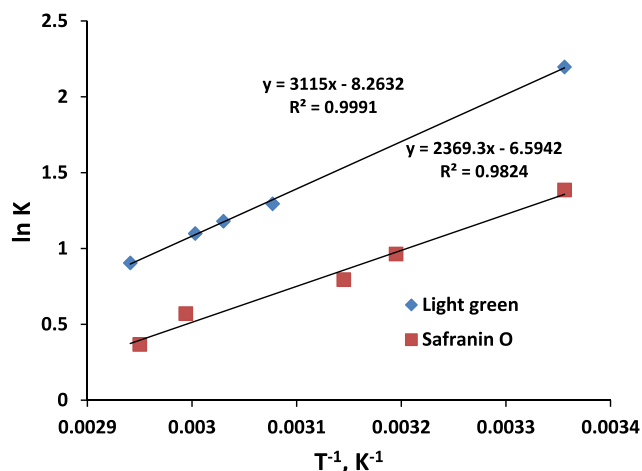
In order to determine the mass of sorbent necessary to concentrate dyes from a given sample, the adsorptive capacity has to be estimated. The plot of amount of adsorbed dye per unit mass of Miswak (Q_c) against initial dye concentration yield perfect linear curves with zero intercept (0.0035) and good determination coefficient ($R^2 = 0.984$). The sorption capacities of Miswak for Light green and Safranin O were estimated to be 0.34 and 1.05 mmol g^{-1} , respectively (252.0 and 365.9 mg g^{-1}). It is evident from the achieved results that the developed sorbent exhibits greater capacity toward Safranin

Table 2 Comparison of the pseudo-first-order and pseudo-second-order models for the sorption of Light green and Safranin O aqueous solution by Miswak.

Dye	Pseudo-first-order			Pseudo-second-order		
	k_1 (min^{-1})	R^2	χ^2	h ($\text{g mmol}^{-1} \text{min}^{-1}$)	R^2	χ^2
Light green	0.16	0.899	0.32	0.002	0.977	0.02
Safranin O	3.53	0.924	0.35	0.017	0.982	0.03

Table 3 Comparison of maximum sorption capacities of various biosorbents for dye removal.

Biosorbent	Q_{\max} (mg/g)	Reference
Coniferous pinus bark	32.8	Ahmad (2009)
Tomato plant root	94.3	Kannan et al. (2009)
Japonica	82.8	Wang et al. (2008)
Skin almonds waste	85.5	Atmani et al. (2009)
Grapefruit peel	254.2	Saeed et al. (2010)
Calotropis procera	4.1	Ali and Muhammad (2008)
Coffee husks	90.1	Oliveira et al. (2008)
Orange peel	14.3	El Nemr et al. (2009)
Wheat straw	227.3	Gonga et al. (2008)
Miswak	252.0 and 365.9	This work


Figure 5 Freundlich adsorption isotherm for the adsorption of Light green and Safranin O by Miswak.

Figure 6 Plot of $1/T$ vs. $\ln K$ for the adsorption of Light green and Safranin O by Miswak.

O than Light green, which indicates that the sorption capacities of the dyes depend on the size of the dye molecule. The sorption capacity of Miswak is compared with other biosorbents (Ali and Muhammad, 2008; El Nemr et al., 2009; Ferrero, 2007; Gonga et al., 2008; Mohamed, 2004; Oliveira et al., 2008; Ozacar and Sengy, 2004); the Miswak exhibits better capacity values in comparison to biosorbents (Table 3).

The data from the sorption isotherms were analyzed using Freundlich ($\log Q_c = \log K_F + \frac{1}{n} \log C_e$); Langmuir [$C_e/Q_c = (1/K_L b) + (C_e/K_L)$] and Dubinin Radushkevich ($\ln Q_c = \ln K_{D-R} - \beta \varepsilon^2$ & $\varepsilon = RT \ln [1 + (1/C_e)]$) equations, where C_e is the amount of dye adsorbed at equilibrium. K_F , n , K_L , b , ε , β and K_{D-R} are constants.

The plot of Q_c/C_e vs. C_e for the experimental data according to Langmuir model give a bad linear relationship ($R^2 = 0.28$). These models suggested that sorption of dyes

from solution by the PPF is monolayer coverage. The linear plot of $\log Q_c$ vs. $\log C_e$ ($R^2 = 0.913$, Fig. 5) is shown; this enabled determination of the Freundlich constants ($1/n$) from the slope of the plot. The $1/n$ values for sorbed Light green and Safranin O were 0.96 and 0.84, respectively, which may be attributed to the heterogeneous surface structure of the Miswak (Table 4). In addition, the values of n are 1.04 and 1.19 for the tested dyes, indicating that the sorption is favorable.

The Dubinin-Radushkevich isotherm was tested. The linear plot ($R^2 = 0.916$) of $\ln Q_c$ vs. ε^2 is shown. Both the values of β for sorption of Light green and Safranin O computed from the slope are $-0.006 \text{ kJ}^2 \text{ mol}^{-2}$. The value of the sorption energy (activation energy, E) can be correlated with β ($E = 1/\sqrt{-2\beta}$). The value of E evaluated is 9.13 kJ mol^{-1} . The small values of E indicate that the rate of sorption is relatively fast.

Table 4 Langmuir and Freundlich isotherm model parameters, and their respective correlation coefficients for the sorption of Light green and Safranin O aqueous solution by Miswak.

Dye	Langmuir			Freundlich		
	K_L (mg g ⁻¹)	b (L mg ⁻¹)	R^2	K_F (mg g ⁻¹)	$1/n$	R^2
Light green	71.4	0.005	0.029	231.2	0.96	0.860
Safranin O	76.9	0.014	0.537	149.3	0.84	0.966

3.2.4. Thermodynamic investigations

The effect of temperature on the sorption of Light green and Safranin O onto Miswak was studied. It showed that the sorption of dyes decreases with increasing the temperature. The decrease in dye sorption onto Miswak is due to the deformation of bonds between the dye molecules and the active site of Miswak.

Thermodynamic parameters for the adsorption of Light green and Safranin O were calculated using the equations: $\ln K = -\Delta H/RT + \Delta S/R$, $K = ((C_o - C)/C)$ and $\Delta G = \Delta H - T\Delta S$ where K is the distribution coefficient for sorption. The linear plots of $\ln K$ vs. $1/T$ ($R^2 = 0.991$, Fig. 6) give the numerical values of enthalpy (ΔH) and entropy (ΔS) from the slope and the intercept, respectively. The values of ΔH for the sorption of Light green and Safranin O are -25.95 and $-19.7 \text{ kJ mol}^{-1}$, respectively. The values of ΔS are -68.6 and $-54.7 \text{ J K}^{-1} \text{ mol}^{-1}$ for sorbed of Light green and Safranin O, respectively. The values of free energy (ΔG) are -5.51 and $-3.39 \text{ kJ mol}^{-1}$ for Light green and Safranin O, respectively. The negative values of the entropy may be indicative of the faster adsorption of tested dyes onto Miswak. The negative values of ΔG and ΔH for the sorption of Light green and Safranin O onto Miswak are attributed to the spontaneous nature of sorption and exothermic process.

4. Conclusion

The present work deals with the preparation of new biosorbent (Miswak) and it was used for removal of acid and base dyes from aqueous solutions. Characterization of the Miswak indicates the presence of phenolic, carboxylic, lactonic and amino groups in the Miswak matrix. The kinetics and thermodynamics of the Light green and Safranin O dyes sorption onto Miswak were studied. The negative values of ΔG and ΔH indicate the spontaneous and exothermic nature of the sorption of dyes. From our study, we can conclude that Miswak has the ability to remove acidic and basic dyes from water sample.

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