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Effect of heating processes on *Salvadora persica* (Miswak) and its application for removal and determination of aniline blue from wastewater

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Abstract

Effect of heating processes of *Salvadora persica* (Miswak) with different temperature (308, 378 and 523 K) on the Miswak matrix was studied. Miswak after heating was characterized using different tools such as elemental analysis, IR spectroscopy, nuclear magnetic resonance and scanning electron microscopy. The sorption properties of Miswaks behavior for removal of aniline blue from aqueous solution were investigated using a batch processes. The maximum uptake of aniline blue was found to be in pH range 1–2. The kinetic behavior of the sorption of the aniline blue was found to be fast with average values of half-life of sorption ($t_{1/2}$) of 30 s. The equilibrium process is well described by the Freundlich isotherm model, which attributed to the heterogeneous surface structure of the Miswak. The average capacity of the Miswak material was 0.37 mmol/g for aniline blue dye. The average values of thermodynamic parameters, ΔH and ΔG are -14.7 and -31.7 kJ/mol, respectively. The sorption data indicates that the sorption of aniline blue onto Miswak proceed via both solvent extraction and ion association mechanism. Miswak was verified as a good biosorbent by aniline blue removal from wastewater.

Keywords: *Salvadora persica*; Miswak; Removal; Aniline blue; Biosorbent

1. Introduction

The removal of dye from wastewaters before their discharge is essential for environmental safety [1–3]. Recently, scientists have developed low cost, efficient and effective adsorbents of biological nature and mineral matrix to remove dyes in simulated liquid effluents of industry. They reach a conclusion that among the studied materials features revealed promising potential [4–6]. Biosorption technique is one of the most efficient methods used for the removal of contaminants from wastewater [7–9]. The design and efficient operation of biosorption process has been found to be effective and cheap [10–12]. A variety of agricultural biomass has been used for biosorption process, e.g. pyracantha coccinea [10], orange peel [11], bottom ash [12], olive pomace [13], phaseolus vulgaris [14], symphoricarpus albus [15], cypress cone chips [16], beech [17], peat [18], pinus bark powder [19], tomato plant root [20], deoiled soya [21], alligator weed, japonica, rice bran, wheat bran [22], waste rubber tire [23], treated

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alga [24] and skin almond waste [25]. However, new, economical, locally available and highly effective dye biosorbents are still needed to investigate for the scavenging of dye from wastewater. Agricultural products are complex materials containing cellulose and lignin as major constituents. Chemical adsorption can occur by the polar functional groups of lignin, which include alcohols, aldehyde, ketone, phenolic hydroxides and ethers that could increase the affinity of the sorbent material towards organic molecules.

Salvadora persica (Arak, Miswak and toothbrush tree) is a small tree 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. *S. persica* sticks were 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 [26–28]. The stick of Miswak consists mainly of cellulose, hemicelluloses and lignin. The lignin content in the pulp is higher than its content in the outer layers [29]. In this work, we studied the effect of temperature (heating processes) on Miswak matrix. In addition, the sorption behavior of aniline blue dye onto the Miswak has been studied to optimize the conditions for the best removal of dye from aqueous solution. The data has been obtained for kinetic, thermodynamic, and equilibrium situations.

2. Materials and methods

2.1. Reagents and materials

Aniline blue dye ($C_{37}H_{32}N_5O_9S_3$, 786.9 g/mol) was purchased from BDH (Poole England). A 1 mg/mL stock solution of Aniline blue was prepared by dissolving 0.1 g of pure dye in 100 mL of water.

The raw biosorbent of Miswak were obtained from a plantation in El-Khtrichia, Saudi Arabia. The sticks of Miswak were washed by tap and distilled water to remove impurities such as sand. Miswak-1, Miswak-2 and Miswak-3 were prepared by drying of Miswak sticks at 35, 105 and 250 °C, respectively for 24 h. Then the dried sticks were blended in a food-processing blender. The Miswaks powder was sieved to obtain biosorbent with homogenous known particle size. The particles between 90 and 250 μm were used for adsorption studies. The photo of the Miswak-1, Miswak-2 and Miswak-3 powder was shown in Fig. 1.

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. NMR spectra were measured with a 500 MHz spectrometer using a JEOL JNM-LA

Fig. 1. Photo of Miswak powder at 35, 105 and 250 °C.

Table 1
Effect of heat treatment on the property *Salvadora persica* (Miswak).

Property	Miswak-1	Miswak-2	Miswak-3
Heat treatment (K)	308	378	523
Colour	Pale yellow	Brown	Black
% Weight losses	4.54	22.3	64.4
Density (g/cm^3)	0.39	0.48	0.67
Conductivity (1%) (mS/cm)	2.69	2.89	5.04
pH (1% solution)	5.35	6.30	7.66
pH_{ZPC}	4.50	5.17	7.28
Iodine number (mmol/g)	0.73	0.84	1.31
C, H, N and S (%)	28.3, 4.6, 2.1 and 3.3	33.2, 5.0, 2.6 and 4.8	30.4, 1.5, 2.9 and 8.4
IR spectra			
υ —OH, —NH_2 and —COOH (cm^{-1})	3600–3000	3600–3000	Disappeared
υ —CH aliphatic (cm^{-1})	2926.8	2926.2	Disappeared
υ C=C (cm^{-1})	1624.7	1612.0	1572.8
υ C—C (cm^{-1})	1016.2	1017.6	1087.8
^{1}NMR spectra			
Aliphatic —CH_2, —CH_3 (ppm)	1.25 and 1.86	1.25 and 1.82	1.54
Alcoholic and phenolic —OH (ppm)	2.58 and 4.50	2.58 and 4.50	Disappeared
Aryl protons Ar—H (ppm)	7.27	7.27	7.26

500 FT-NMR System. The pH meter (Jenway, model 3510, UK) used in the pH measurements. Conductivity measurements were performed on a Conductivity Meter 4071 (Jenway, UK).

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. Aniline blue concentration was estimated spectrophotometrically by monitoring the absorbance at 599 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. The following equations were used to calculate the removal percentage of dye (%E) and capacity of sorbents (Q, mg/g):

$$\%E = \left(\frac{(C_o - C)}{C_o}\right) \times 100 \quad (1)$$

$$Q = \frac{(C_o - C)V}{m} \quad (2)$$

where C_o and C are the initial and remain concentrations of dyes in solution, respectively. V is the volume of solution and m is the mass of sorbent.

Zero point charge pH (pH_{ZPC}) is the pH at which the charge on the Miswak surface is zero. To determine the pH_{ZPC} of the Miswak surface, 25 mL of the solution was added to a series of 100 mL flasks with pH in the range of 1–13. The initial pH (pH_i) of the solutions was determined and 0.1 g of the Miswak was added to each flask. After 24 h, the final pH (pH_f) of the solutions was measured. The difference between the initial and final pH values ($\Delta pH = pH_f - pH_i$) was plotted against the pHi. The pH_{ZPC} was noted as the pH at which the initial pH equals the final pH.

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 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.

3. Results and discussion

3.1. Effect of heating process on the Miswak matrix

The effect of heating process on the weight of Miswak was studied. The percentage of weight losses of Miswak after 24 h is 4.5–64.4% (Table 1). The result obtained shows that the weight of the Miswak was decreased after heating and the percentage of the weight losses was increased with the increasing of the temperature (Table 1). In addition, these results indicate that some groups of Miswak were hydrolyzed with heating processes.

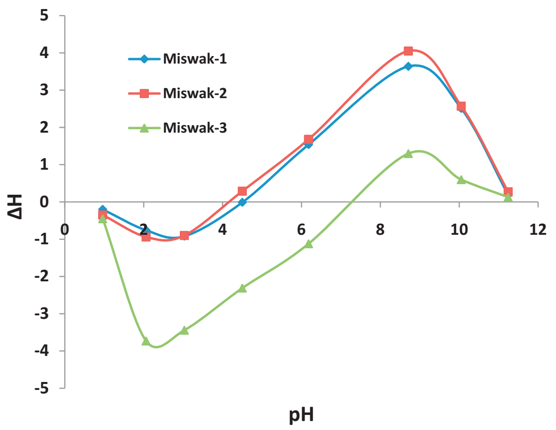

Fig. 2. Zero point charge pH (pH_{ZPC}) of Miswaks powder.

The densities of the Miswak after heating were measured. The values of densities increased from 0.39 to 0.67 g cm^{-3} with the increasing of the temperature from 308 to 523 K (Table 1). These results confirm that the particle size of Miswak decreased.

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 values of electrical conductivity were 2.7, 2.9 and 5.0 mS/cm for 1% solution of Miswak-1, Miswak-2 and Miswak-3, respectively. Miswak-3 has higher conductivity than Miswak-2 and Miswak-1. The result could be attributed to high content of dissolved ions (due to increasing in sulphate salts) and polar compounds in Miswak-3.

The pH of Miswaks suspension was measured to investigate the change in pH due to any soluble species from the Miswaks material in water. The sample (1%, w/v) was shaken in distilled water for 3 h and then the pH was measured. The pH values obtained were 5.4, 6.3 and 7.7 for Miswak-1, Miswak-2 and Miswak-3, respectively. These results indicate that mainly the material of Miswak-1 and Miswak-2 has acidic effect while Miswak-3 is basic in character.

The pH_{ZPC} value was determined to be approximately 4.5, 5.2 and 7.3 for the Miswak-1, Miswak-2 and Miswak-3, respectively (Fig. 2). At pH lower than the pH_{ZPC} ($pH < pH_{ZPC}$), the surface of the Miswak is positively charged while at pH greater than pH_{ZPC}, the surface of the Miswak becomes negatively charged.

The iodine adsorption capacity (Q) was determined from the adsorbed iodine/unit mass of the adsorbent at the residual iodine concentration (Table 1). The capacity sequence was in the order of Miswak-3 > Miswak-2 > Miswak-1, which depends on the number of pores per gram of Miswak ($Q_{\text{Miswak-3}} \approx 2Q_{\text{Miswak-1}} \approx 1.6Q_{\text{Miswak-2}}$) and the density of Miswak-3 > 1.7-fold of Miswak-1 and 1.4 of Miswak-2. It is found that the Miswak exhibits better capacity values when compared with biosorbents. The average sorption capacity of Miswak is 0.96 mmol/g while the capacities of pine cone, jatropha husk and coir pith carbon are 0.13, 0.55 and 0.80 mmol/g, respectively [30–32].

The infrared spectra of the Miswak-1, Miswak-2 and Miswak-3 were tested using thin KBr technique. FT-IR measurement for the Miswak-1 showed the presence of the following groups: –OH, $-NH_2$ and –COOH (a broad absorption between 3600 and 3000 cm^{-1}), –CH aliphatic (2926.8 cm^{-1}), C=C aromatic (1624.7 cm^{-1}), –NH (1524.7 cm^{-1}) and C–C (1016.2 cm^{-1}) (Table 1). The spectra of Miswak-2 showed that the bands at 1524.7 and 1427.5 cm^{-1} ate shifted to 1612.0 and 1408.8 cm^{-1}. The bands at 1524.7, 1358.2 and 1235.3 cm^{-1} disappeared. While, the spectra of Miswak-3 contains only two bands at 1572.8 and 1087.8 cm^{-1} characteristic of C=C aromatic and C–C aliphatic groups, respectively.

The elemental analysis of Miswaks sample was determined. The sulphur and nitrogen percentage increased with increasing of temperature (Table 1). The hydrogen and carbon percentage increased then decreased with increasing of temperature. The results show that the change of carbon and hydrogen percentage with heating is due to decreasing of molecular weight of Miswak compounds. Disappearing of –OH and –COOH bands in the spectra of Miswak-3 indicates the loss of H_2O and CO_2 molecules. While sulphur and nitrogen compounds had turned to mineral salts.

^{1}H NMR spectra for the Miswaks dissolved in $CHCl_3$ is listed in Table 1. In the spectra of Miswak-1 and Miswak-2, two characteristic peaks were observed at 1.25 and 1.86 ppm standing for the chemical shifts of H in aliphatic –CH. Two single peaks attached were observed at 2.58 and 4.50 ppm due to aliphatic –OH and phenolic –OH, respectively. In addition, single peak at 7.28 ppm had appeared which imply the H of target compound belongs to aryl protons (Ar–H). While, only two bands at 1.54 and 7.26 ppm characteristic CH aliphatic and aromatic had appeared in the spectra of Miswak-3.

The surface morphology of Miswaks powder was investigated by scanning electron microscope (SEM) at magnification of 1500. The SEM images of Miswak are shown. The microstructure of Miswaks image showed that the surface could be seen to contain amounts of small pores indicating that this material has good characteristics to be employed as a natural adsorbent for dye uptake (Fig. 3). The microstructure of Miswaks showed that the cells are nearly spherical and irregular in size and

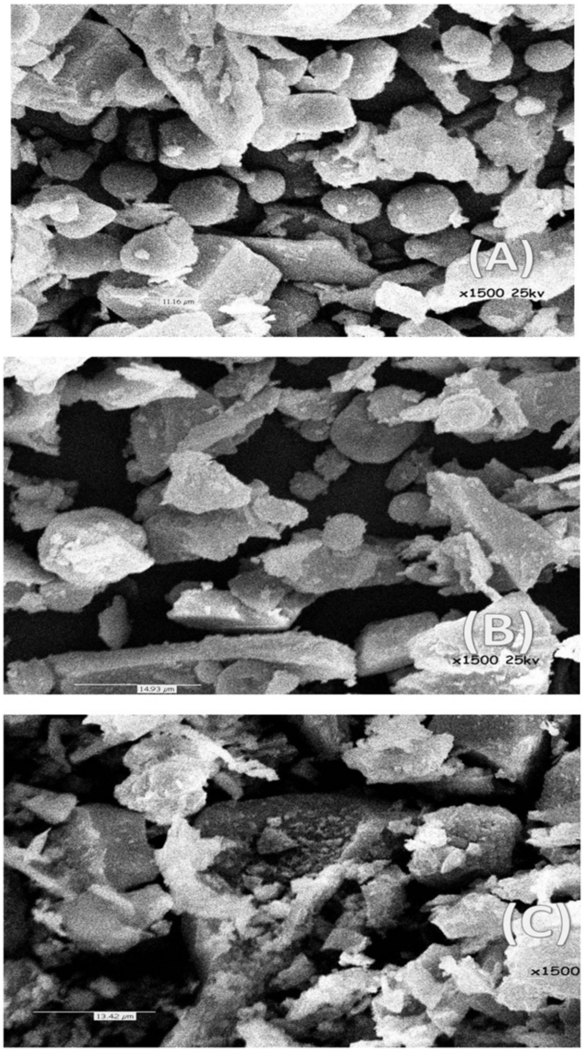

Fig. 3. SEM images of Miswaks powder: (A) Miswak-1; (B) Miswak-2; (C) Miswak-3.

distribution. The cell size of Miswak-3 is found to be bigger than that of Miswak-1 and Miswak-2. It is believed that these pores provide ready access and large surface area for the sorption of dyes on the binding sites.

3.2. Optimum condition for removal of aniline blue

The effect of pH on the sorption of aniline blue dye (Fig. 4) onto different types of Miswaks was examined. The removal percentage of aniline blue was plotted against the pH. The results show that the optimum pH for the maximum sorption of dye onto Miswak-1, Miswak-2 and Miswak-3 occurs in 1-2, 1 and 1-9, respectively. At pH between 1 and 4.5-5.2, the increase in positively charged Miswak-1 and Miswak-2 sites as pH decreases

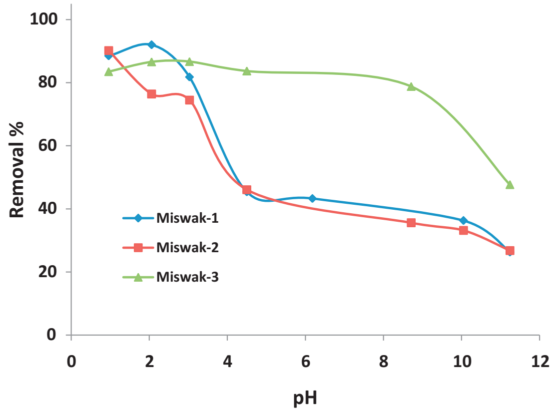

Fig. 4. Effect of pH on the sorption of aniline blue onto Miswaks.

led to the increase of electrostatic attraction between the surfaces positive charges and the negatively charged aniline blue molecules and therefore to the increase of the sorption percentage of aniline blue. While the Miswak-1 and Miswak-2 surfaces become negatively charged at pH greater than 4.5-5.2 and the negatively charged surface groups increase as pH increases. Accordingly, an electrostatic repulsion between the negatively charged dye and surface groups took place and led to a significant decrease of the sorption of aniline blue. The wide range of pH values (1-9) for the sorption of aniline blue onto Miswak-3 indicates that the sorption of the dye is independent on the polarity of Miswak-3 surface.

Kinetic measurements were carried out using Miswaks powder, which has a diameter 0.09-0.25 mm with batch factor (volume of sample/mass of Miswak) 250 mL g^{-1} by batch extraction mode at different time intervals. From the results obtained, the required time for sorption equilibrium of aniline blue onto Miswak-1, Miswak-2 and Miswak-3 was found to be 10, 5 and 0.5 min, respectively. This rapid extraction is due to the sorption of dye, which is relatively fast as compared to the other dye [3,9].

The sorption of aniline blue on Miswaks depends on three transport processes: bulk transport of solute in solution, film transfer involving diffusion of solute through a hypothetical film boundary layer and diffusion of the solute within the pore volumes of the adsorbent and along pore-wall surfaces to active adsorption sites. In this regard, the Bangham ($\log\log(C_o/C_o - Q_t m) = \log(k_o m/2.303V) + \alpha \log(t)$), Reichenberg equations $Q_t/Q_e = 1 - 6\pi^{-2} e^{-Bt}$ where $B = \pi^2 r^{-2} D_i$ and Morris–Weber ($Q_t = k_i\sqrt{t}$) models are applied to explain the diffusion mechanism of aniline blue onto Miswaks. For the pore diffusion mechanism, the kinetic data for the sorption of aniline blue onto Miswaks

Table 2
Diffusion parameters for the sorption of aniline blue onto Miswaks.

Sorbent	Bangham model		Reichenberg model		Morris–Weber model	
	α	R^2	D_i	R^2	k_i	R^2
Miswak-1	0.32	0.839	0.001	0.895	0.06	0.921
Miswak-2	0.13	0.903	0.002	0.929	0.04	0.980
Miswak-3	0.91	0.920	0.011	0.987	0.38	0.848

were analyzed by using Bangham model. The linearity ($R^2 = 0.887$) of the double logarithmic plot for the Bangham equation shows that the diffusion of dye into pores of the Miswak is the rate controlling step. The Q_t was plotted against the square root of time to test the applicability of the Weber–Morris equation. The obtained results show the rate of diffusion is fast in the early stages of sorption and a linear relationship ($R^2 = 0.916$) was verified where the diffusion constant (k_i) was found to be 0.16 μmol g^{-1} $min^{-1/2}$. The k_i values sequence were in order Miswak-3 > Miswak-1 and Miswak-2 which indicate that these values depends on the molecular pore size of Miswak. For the film diffusion controlled kinetics, the expression developed by Boyd and improved by Reichenberg model was applied. The plot of B_t versus t is straight lines that do not pass through the origin indicating that mass transfer is the rate limiting step. The linearity of this plot will provide useful information to distinguish between external transport and intraparticle transport controlled rates of sorption. In addition, the values of the effective diffusion coefficient (D_i) has increased with the increasing of the particle pore size of Miswaks, Miswak-3 > Miswak-2 > Miswak-1 (Table 2). This reflects that the film diffusion rate depends on the pore size of Miswak.

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 aniline blue onto Miswaks. Table 3 contains the comparing between the values of correlation coefficient (R^2) values for pseudo second order and pseudo first order models. The R^2 values for pseudo second order sorption model are higher than the values of R^2 for pseudo first order kinetic in case of Miswak-1 and Miswak-2. This suggests that the pseudo second order adsorption mechanism is predominant. While the value of R^2 value (0.987) for pseudo first order sorption model is higher than R^2 value for pseudo second order kinetic (0.910). Therefore, the pseudo first order adsorption mechanism is predominant for the sorption of aniline blue onto Miswak-3 (Fig. 5). This result indicates that the sorption kinetic depends on the Miswak type.

Table 3
Kinetic parameter of pseudo first order and pseudo second order models.

Sorbent	Pseudo first order model		Pseudo second order model	
	k_1	R^2	h	R^2
Miswak-1	0.44	0.894	2.35	0.997
Miswak-2	0.53	0.932	3.61	0.999
Miswak-3	3.66	0.987	0.91	0.910

The uptake of the aniline blue dye onto Miswaks was determined as a function of dye concentration in the aqueous solution. The resultant isotherms show a good linear relationship, the average values of correlation coefficient (R^2) and intercept are 0.980 and 0.07×10^{-4}, respectively. The isotherm capacity (Q) of the Miswaks for aniline blue using batch technique was calculated, the average values obtained were 0.37 mmol/g (Table 4). The capacity sequence was in the order of $Q_{\text{Miswak-1}} > Q_{\text{Miswak-2}} > Q_{\text{Miswak-3}}$, which depends on the number of polar groups per gram of Miswak. This result is in disagreement with the sorption of iodine onto Miswak, the capacity increases as the pore size of Miswak increases.

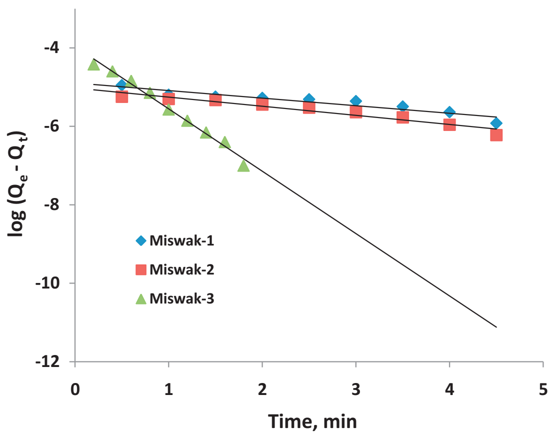

Fig. 5. Linearized pseudo-first-order plot for the sorption of aniline blue by Miswaks.

Table 4
Characteristics of the isotherm curves of the sorption of aniline blue onto Miswaks.

Sorbent	Least square equation		Correlation coefficient (R^2)	Capacity
	Slope	Intercept ($\times 10^{-4}$)		Q (mmol/g)
Miswak-1	0.09	0.012	0.996	0.46
Miswak-2	0.08	0.107	0.986	0.40
Miswak-3	0.05	0.092	0.958	0.26

The results of the aniline blue concentration on Miswaks were analyzed using Dubinin Radushkevich ($\ln Q_c = \ln k_{dr} - \beta\varepsilon^2$ and $\varepsilon = RT \ln[1 + (1/Q_c)]$) equations where Q_c are the amounts of dye sorbed per unit mass of the Miswak. K_{DR}, ε and β are constants. The values of β for sorption of aniline blue onto Miswak-1, Miswak-2 and Miswak-3 are −0.01, −0.005 and −0.002, respectively. The values of sorption energy (activation energy, ΔE) were correlated to β ($E = 1/\sqrt{-2\beta}$). The values of (ΔE) for sorbed of aniline blue onto Miswak-1, Miswak-2 and Miswak-3 are 7.1, 10 and 15.8 kJ/mol, respectively.

The plot of Q_c/C_e vs. C_e for the experimental data according to Langmuir model [$C_e/Q_c = (1/K_L b) + (C_e/K_L)$] give a bad linear relationship ($R^2 = 0.27$) for the sorption of aniline blue onto Miswak-1 and Miswak-1. However, the value of R^2 was 0.785 for the sorption of dye onto Miswak-3. This model suggested that the sorption of dye from aqueous solution to the solid surface is monolayer coverage. The plot of $\log Q_c$ vs. $\log q_e$ was shown in Fig. 6, which allowed the determination of the Freundlich constants (*1/n*) from the slope of the plot of Freundlich model ($\log Q_c = \log K_F + (1/n) \log C_e$). The average value of correlation factor was 0.74, which may be attributed to the heterogeneous surface structure of the Miswak.

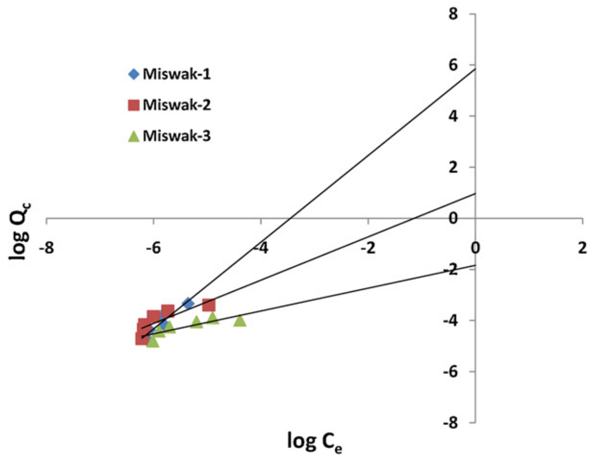

Fig. 6. The plot of $\log Q_c$ vs. $\log q_e$ for the sorption of aniline blue onto Miswaks.

The dependence of sorption of aniline blue onto Miswaks on temperature was studied. The results obtained show that the sorption of aniline blue was better at low than at high temperature. The thermodynamic parameter of the aniline blue sorption onto Miswaks has been evaluated using the equations: $\ln K_C = -(\Delta H/RT) + (\Delta S/R)$ and $\Delta G = \Delta H - T\Delta S$ where K_c is the distribution coefficient for sorption. The linear plots of $\ln K_c$ vs. $1/T$ ($R^2 = 0.95$) give the numerical values of enthalpy ((H) and entropy ((S) from the slope and the intercept, respectively. The values of ΔG, ΔH, and ΔS at 298 K for the sorption of aniline blue are given in Table 5. The average values of (ΔG) are −31.7 kJ/mol and the negative values of ΔG indicate that the sorption process is energetically favorable. Similarly to the negative values of ΔH (−14.7 kJ/mol) are interpreted as the exothermic chemisorptions process. The low activation energy of the sorption as compared to the enthalpy indicates the strong attraction operation during sorption and the uptake process occurs even under normal conditions. The average value of (S is 57.1 J/K mol. The positive value of the entropy may be indicative of the faster adsorption of aniline blue onto Miswak.

Table 5
Thermodynamic parameters of the sorption of aniline blue onto Miswaks.

Sorbent	Free energy ΔG (kJ/mol)	Enthalpy ΔH (kJ/mol)	Entropy ΔS (J/K mol)	Activation energy ΔE (kJ/mol)
Miswak-1	−50.0	−24.0	87.4	7.1
Miswak-2	−21.7	−9.1	42.3	10.0
Miswak-3	−23.5	−11.1	41.7	15.8

4. Method validation

A regression analysis of the calibration curve revealed a good correlation ($r = 0.985$). Also, the values of limits of detection (LOD = 3SD/b, where SD is standard deviation of intercept and b is the slope of the calibration curve) of aniline blue onto Miswak-1, Miswak-2 and Miswak-3 are 7.05×10^{-4}, 5.84×10^{-4} and 5.77×10^{-4}, respectively. Also, the limits of quantitation (LOQ = 10SD/b) are 2.35×10^{-3}, 1.95×10^{-3} and 1.92×10^{-3} for aniline blue onto Miswak-1, Miswak-2 and Miswak-3, respectively. The sensitivity sequence was in order, Miswak-3 > Miswak-2 > Miswak-1, may be attributed to the difference in pore sizes of Miswak. The removal percentage values ranged from 92.0% to 97.9%, with average value of RSD from 7.75% ($n = 3$), which are suitable for the removal of aniline blue using Miswaks.

5. Sorption mechanism

At pH lower than the pH_{ZPC} (4.50 and 5.17), the surfaces of the Miswak-1 and Miswak-2 are positively charged. Therefore the aniline blue molecules are adsorbed due to electrostatic interaction with the positively charged surface of the Miswak-1 and Miswak-2 in acidic medium (pH 1–3). The biosorption mechanism is probably a two step mechanism involving the adsorption of the hydrogen ion from solution onto the biosorbent surface followed by electrostatic attraction between the positive surface and the anionic adsorbate [33]. This can be attributed to the electrostatic attraction between the negatively charged dye and the positively charged surface of Miswak. It could reasonably be suggested that the sorption of aniline blue onto Miswak-1 and Miswak-2 may proceed via ion association. The sorption percentage of aniline blue decreases with the increase of the pH values which results in a decrease in surface charge density indicating this suggestion. The pH_{ZPC} value of Miswak-3 is 7.28 and the sorption of aniline blue onto Miswak-3 is at pH 1–9. In acidic medium (pH 1–3), we suggest the sorption of aniline blue onto Miswak-3 is similar as Miswak-1 and Miswak-2 while at pH 3–9 the sorption of dye is due to solvent extraction mechanisms.

The capacity sequence of the Miswaks for aniline blue was in the order of $Q_{\text{Miswak-1}} > Q_{\text{Miswak-2}} > Q_{\text{Miswak-3}}$, which depends on the number of polar groups per gram of Miswak. This result is in disagreement with the sorption of iodine onto Miswak ($Q_{\text{Miswak-3}} > Q_{\text{Miswak-1}} > Q_{\text{Miswak-2}}$), the capacity increase as the pore size of Miswak increases. These results indicate that the sorption of aniline blue onto the Miswaks is due to the solvent extraction and ion association mechanisms.

6. Conclusion

The present work deals with the effect of heating process of Miswak on the sorption mechanism of aniline blue. Characterization of the Miswak indicates the presence of $-OH$, $-NH_2$ and $-COOH$ groups in aliphatic and aromatic series for the Miswak-1 and Miswak-2 matrix. These groups disappeared in Miswak-3 matrix. The sorption mechanism for the aniline blue from aqueous solution onto Miswak proceeds via both weak solvent extraction and ion association mechanisms. The sorption behavior of aniline blue dye onto the Miswak has been studied to optimize the best conditions for removal of dye from wastewater. In addition, the equilibrium, kinetics and thermodynamics of the aniline blue sorption onto Miswak were studied. The negative values of ΔG and ΔH indicate that the spontaneous and exothermic nature of the sorption of aniline blue dye. From this study, we conclude that Miswak has the ability to remove dye from wastewater.

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