

Removal of Malachite Green Dye from Aqueous Solution by Adsorption Using Modified and Unmodified Local Agriculture Waste

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Abstract: Local agriculture waste (Shell's seeds of *Ziziphus spina christi*) (SZC), in both its unmodified SZC and acid-modified (SZC-AC) forms, was investigated for its potential use as a low-cost adsorbent for the removal of malachite green (MG). Characterization of the adsorbents was carried out using scanning electron microscope (SEM), Fourier transforms infrared spectroscopy (FTIR), pH surface, Boehm titration, including, other physical and chemical properties of adsorbent. The effects of initial dye concentration, contact time, solution of pH, temperature and adsorbent dosage were investigated in detail by batch adsorption experiments. For the adsorption of MG were fitted using Langmuir and Freundlich isotherm models, equilibrium isotherms were applicable with maximum monolayer adsorption capacity wear 48.780 mg/g and 370.370 mg/g for the raw shells seeds of *Ziziphus spina christi* (SZC) and the activated carbon prepared from shells seeds by sulphuric acid SZC-AC, respectively. Kinetics studies showed that both followed the pseudo-second order. Thermodynamics studies indicated that the adsorption of MG was spontaneous on SZC and SZC-AC, and the reactions were endothermic and exothermic, respectively. The proposed adsorbents were successfully applied to the removal of malachite green dye from different water samples with a recovery % >95% and a relative standard deviation (RSD%) <3%.

Keywords: *Ziziphus spina christi*, Malachite Green, FTIR, SEM, Boehm Titration

1. Introduction

Water pollution today is one of the most undesirable environmental problems in the world and it requires solutions [1]. As the overall water demand for grows, the quantity of wastewater produced continuously increasing worldwide, this creates a need for efficient purification methods. Wastewater is often discharged into rivers and lakes or infiltrates into aquifers, where it can affect the quality of freshwater supplies, globally over 80% of the wastewater back into the environment without treatment cause negative consequences for the marine environment [2].

More than 600 organic and inorganic pollutants have been reported in water along with biological pollutants [3]. Among organic contaminants, dyes and coloring agents cause significant environmental harm on both human health and

aquatic organisms. These dyes are high toxicity, carcinogenic, mutagenic, teratogenic, and stable during aerobic degradation [4]. The discharges of industrial wastewater containing very low concentrations of dyes reduce light penetration through the water surface, precluding photosynthesis of the aqueous flora.

At this time, there are nearly 10,000 types of dyes are synthetic, with worldwide annual production of over 7×10^5 tons per year [5]. Malachite green MG is a cationic dye appears as a green crystalline powder that dissolved in water. It is used for the dyeing of cotton, paper, jute, silk, wood, leather products, antiparasitical, antibacterial and antifungal in aquaculture and commercial fish hatchery industries. It is also used as a food coloring agent, food additive, a medical disinfectant, and an anthelmintic. MG dye has caused several health hazards such as damage to nervous system,

brain and liver when ingested, eye burns, fast breathing, profuse sweating and cancer of different parts of the body [6].

Many treatment technologies have been applied to decrease the concentrations dyes from an aqueous media such as adsorption techniques [7], biological treatment [8], decolorization and detoxification [9], photocatalytic degradation [10] and electrochemical degradation [11]. Among treatment strategies, adsorption was regarded to be an effective and preferable method for removing pollutants from wastewater, this method is low cost, the simplicity of design, high removal efficiency, ease of operation and availability. Adsorption is a separation process, in which the number of chemical components being collected (adsorbate) are increased at the surface of a solid (adsorbent).

Agricultural waste have advantages as adsorbents: readily available and exist in abundance, they are cost-effectiveness, renewable, require less processing time, offer suitable adsorption capability and can easily be regenerated [12]. Agricultural waste can be modified by treating it with different chemical agents *eg.*, alkalis, acids, organic compounds, *etc.*, or thermally, this modification could have beneficial effects on chemical/physical properties including increasing surface area, improve pore structure, adding a functional group. Modified adsorbents exhibit adsorption capacity, more selective and sensitive [13]. Many agricultural

wastes such as cotton stalk [14], olive stones [15], coconut shell [16], rice husk [17], orange peel [18], pistachio shell [19] and wheat bran [20] that used in adsorption applications.

Ziziphus spina christi seeds were used as raw material to prepared activated carbon by Omri and Benzina [21]. The activated carbon was obtained by using KOH as chemical activation in the ratio 3/4/1(w/w) a water/KOH/coal at 700°C carbonization temperature and 120 min. activation time. The results of liquid phase adsorption experiments revealed that the prepared activated carbon is a suitable adsorbent for copper from aqueous solutions with maximum capacity value is 104.16 mg/g.

Local agriculture waste shell's seeds of *Ziziphus spina christi* is used in this investigation to preparing adsorbents, it grows abundantly in arid land regions in Hadhramout – Yemen, Figure 1. The aim of this investigation is to test the adsorption efficiency of MG from aqueous solution and some water samples onto raw shells seeds of *Ziziphus spina christi* (SZC) and activated carbon prepared from shells seeds of *Ziziphus spina christi* by sulphuric acid (SZC-AC). The various analytical factors affecting the removal of dyes are investigated as pH, the dose of adsorbent, the initial concentration of dye, the temperature and the contact time. However, the adsorption kinetic, thermodynamic and isotherm studies were determined to foresee the sorption behavior.



Figure 1. Shell's seeds of *Ziziphus spina christi* a. before grinding, and b. after grinding.

2. Experimental Part

2.1. Materials

Malachite green (MG) dye, basic green, IUPAC name 4, [4-[[4-(Dimethylamino)phenyl]-phenylmethylidene]cyclohexa-2,5-dien-1-ylidene]-dimethylazanium; 2-hydroxy-2-oxoacetate; oxalic acid, C.I. 42000; used as an adsorbate,

was purchased from Merck, chemical formula, $C_{54}H_{54}N_4O_{12}$, molecular weight, 927.00 g/mol, and λ_{max} : 616 nm. Chemical structure of malachite green dye is shown in Figure 2. A 1000 mg/L stock solution of MG dye was prepared by dissolving the required amount of dye in distilled water. A calibration standard curve was constructed using a UV spectrophotometer at a maximum wavelength in rang 1.00 – 10.00 mg/L.

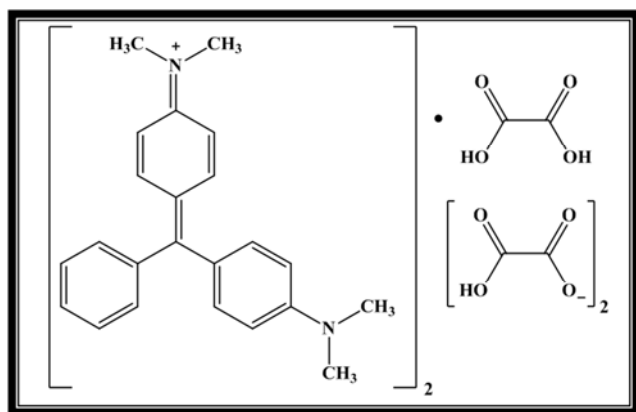


Figure 2. Molecular structure of Malachite green MG.

2.2. Equipments

The concentrations of MG dyes were determined using JASCO V-750 UV-Vis spectrophotometer was used to determine the concentrations of MG dyes. The pH of the solution was adjusted by OAKTON pH-meter 10N 700. Fourier Transform Infrared FTIR spectroscopy 4000-400 cm^{-1} JASCO 4600 FTIR spectrometer. Adsorbent weight was measured using a AND GR 200 electronic balance. These instrumental analyses and experiments were done at PCB Research Laboratory, Faculty of Science, Hadhramout University, Mukalla, Hadhramout, Yemen. The nitrogen adsorption-desorption isotherms were obtained on surface analyzer QUANTACHROME – NOVA 2000. Series were used to measurement of the specific surface area of adsorbent and Scanning electron microscopy JEOL - JSE - T20 in Egypt.

2.3. Preparations of Adsorbents

Shells seeds of *Ziziphus spina christi* for preparation of adsorbents were collected from trees of *Ziziphus spina christi* in Hadhramout – Yemen. The raw materials were first washed repeatedly in order by distilled water to remove dirt and undesirable material from the surface and was then dried in an oven at 110°C until a constant weight was reached. A part of dried raw materials was crushed and milled for use as raw adsorbent and termed SZC, another part was mixed with H_2SO_4 in a 3:1 weight proportion. The mixture was carbonized at $150\text{--}200^{\circ}\text{C}$, for 4 hr, using a heating rate of $10^{\circ}\text{C}/\text{min}$. After the carbonization the samples, air flow was used to cool it, then were washed with distilled water at room temperature until the pH value of washed solution became 5-6. Finally, all samples were dried at 100°C until a constant weight was reached. The percentage yield from prepared activated carbon SZC-AC was calculated from the following, Equation (1):

$$\text{Yield \%} = \frac{W_{tf}}{W_{ti}} \times 100 \quad (1)$$

Where W_{tf} , W_{ti} the mass of the resulting activated carbon SZC-AC and the initial mass of the raw, respectively.

2.4. Adsorption Studies

All batch adsorption experiments were executed on shaking water bath carried out using shaker water bath at 100 rpm, 0.05 g of adsorbent / 50 mL of adsorbent solution put in 200 mL Erlenmeyer flasks closed with glass stoppers to avoid evaporation, the dye solutions were shaken at contact time, to determine the adsorption capacity of adsorbents, using variable concentrations of MG between 5-85 mg/L for SZC and between 80-550 mg/L for SZC-AC, to determining the period required to reach the adsorption equilibrium, time duration of shaking ranged between 15 min and 480 min, the influence of pH on elimination of MG was studied at pH range 2.0-10.0 using 0.01 mol/L NaOH or HCl solution, doses of adsorbent 0.025-0.18 g, the temperatures between 25°C and 50°C and ionic strength between 0.00-0.10 N of NaNO_3 and NaCl. The capacity of adsorption of MG removed by adsorbent q_e and the removal percentage R% of dye is determined by the following equations (2) and (3):

$$q = \frac{(C_o - C_e)}{m} \times V \quad (2)$$

$$R\% = \frac{(C_o - C_e)}{C_o} \times 100 \quad (3)$$

Where q : mg/g is the equilibrium concentration of adsorbate on the adsorbent, C_o : mg/L is the initial dye concentration, C_e : mg/L is the dye concentration at equilibrium, m : g is the mass of adsorbent and V : L is the volume of solution.

3. Results and Discussion

3.1. Characterization of Adsorbents

3.1.1. Surface Area Measurements

The surface area and porosity of adsorbents were estimated using liquid N_2 adsorption at 77°C . Specific surface area was estimated by the BET method (Brunauer–Emmet–Teller) the micropore size distribution, pore diameter and total pore volume obtained from the BJH methods (Barrett–Joyner–Halenda). Figure 3 shows the nitrogen adsorption-desorption isotherms and the pore size distributions of the adsorbent. Figure 3a Indicating both SZC and SZC-AC have plenty of micropores. It was exhibited an additional hysteresis loop at relative pressures indicating it has a significant amount of mesoporous [14, 22].

Almost pore diameter of adsorbent distribution less than 2 nm Figure 3b so that the porosity of SZC and SZC-AC are dominated by micropores [23]. This is verified by the derived textural properties shown in Table 1 and the SEM in Figure 4. Table 1 shows the value of the surface area (S_{BET}), total pore volume (V_t) and average pore diameter (r) for the adsorbents. Specific surface area shows that SZC-AC has a higher BET specific surface area than SZC. The value S_{BET} of SZC-AC is appropriate comparative to other reports that used H_2SO_4 as an activation agent [19, 24].

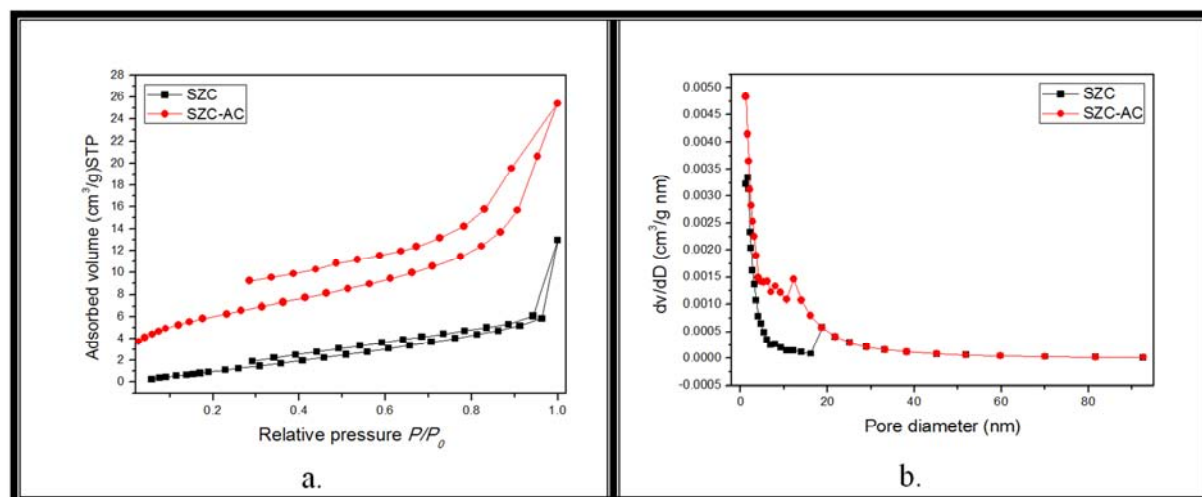


Figure 3. Nitrogen adsorption-desorption curves a. and pore size distributions b. of adsorbents.

Table 1. Textural properties of SZC and SZC-AC.

adsorbents	S_{BET} (m^2/g)	V_t (cm^3/g)	r (nm)
SZC	8.644	0.017070	1.66
SZC-AC	21.493	0.03779	1.22

3.1.2. Scanning Electron Microscopy Analysis SEM

Scanning electron microscopy SEM has been a primary

tool for characterizing the surface morphology of the adsorbents [25], the morphology of the adsorbent surfaces was investigated using scanning electron microscopy JEOL - JSE - T20 in Egypt. SEM image of the SZC is shown in Figure 4(a,b), while the SEM image of SZC-AC, Figure 4(c,d) have large and well cavities and voids compared to the SZC. So, that there is a good possibility for removal dye.

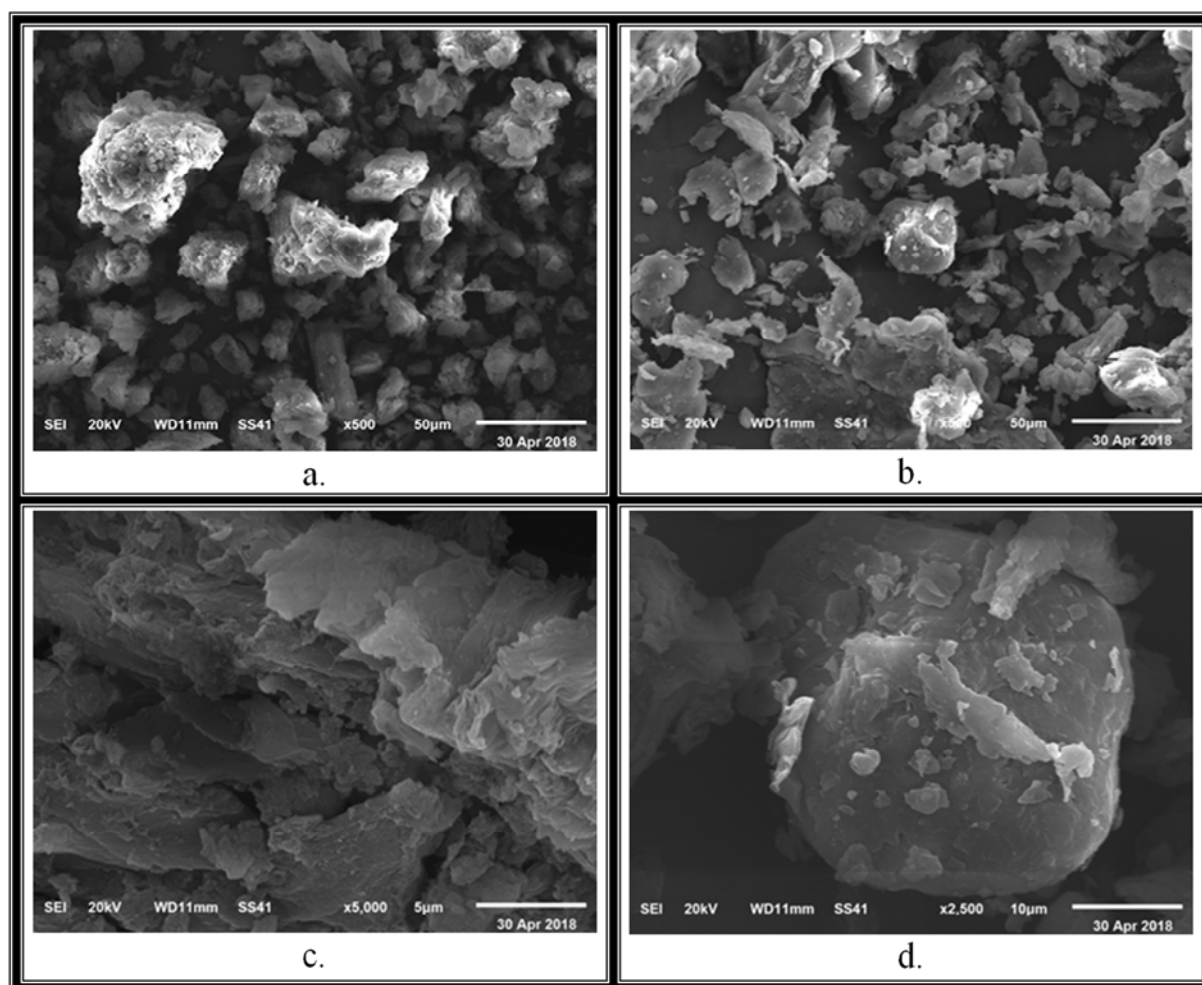


Figure 4. SEM micrograph of SZC (a,b) and SZC-AC (c,d).

3.1.3. FTIR Analysis

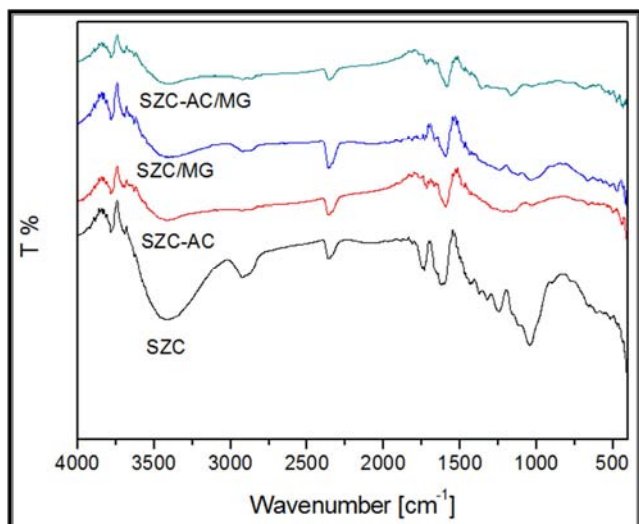


Figure 5. FTIR spectra of SZC and SZC-AC before and after dye adsorption.

Infrared spectroscopy is powerful tool for identifying different types of chemical bonds, and thus functional groups on the surface of the material. Figure 5 shows the FTIR spectrum of the SZC, SZC-AC, SZC/MG and SZC-AC/MG, which indicated various surface functional groups. The FTIR spectrum of the SZC has a peak at about 3435 cm^{-1} resulted from O-H stretching vibrations in alcohol carboxylic acids or phenol [26]. This peak observed in the higher energy region 3448 cm^{-1} and has less intense in SZC-AC. Hence, the water content is also reduced. The low-frequency values for these band suggest that the hydroxyl groups are involved in hydrogen bond. Two peaks were observed at 2909 and 2848 cm^{-1} attributed to stretching vibrations of C-H aliphatic

bonding observed in SZC. The carbonization by sulfuric acid is also very clear by the decrease in the intensity of C-H after carbonization [27].

The spectra of SZC and SZC-AC has a peak at 1681 cm^{-1} assigned to stretching vibrations of C=C aliphatic [19]. The phenolic C=C vibrations appear at 1600 cm^{-1} in SZC and SZC-AC spectrum, these peaks appear at 1567 and 1570 cm^{-1} in SZC-AC spectrum. The small band at about 1718 cm^{-1} are attributed to the existence of C=O stretching vibrations of ketones, lactones and carboxyl groups [28]. The bands at 2330 and 3320 cm^{-1} could be assigned to stretching vibrations in alkynes as acetylenes [29]. The SZC spectrum appears bands in the $1000\text{--}1384\text{ cm}^{-1}$ region assigned to C-O stretching in a carboxylic acid, alcohols and phenols [15]. The spectrum of SZC/MG and SZC-AC/MG shows there is no real shift in our absorption peaks, this is indicated as physical adsorption [26].

3.2. Physical Properties

The bulk density of the prepared adsorbate was measuring by weighing 5 mL of the adsorbent sample using cylinder [30]. The moisture content percent was determined using an oven drying method [31]. The ash content analysis for the adsorbents was determined by heating 0.30 g of samples in crucibles at 600°C using the electrical furnace for 6 hr [32]. The results of the textural properties of adsorbents are listed in Table 2. The SZC-AC has a lower bulk density and the moisture percent than SZC that attributed to after activation process the porosity on SZC-AC surface increases, therefore it is useful for adsorption which it has a high ash content, due to activating agent is dehydrates and decomposition molecules in the raw material and inhibited the formation of ash [33].

Table 2. Physical characteristics of SZC and SZC-AC adsorbents.

Adsorbents	Bulk density g/mL	Moisture content %	Ash content %	Yield%
SZC	0.78	46.5	1.6	-
SZC-AC	0.456	57.8	3.6	76.65

3.3. Chemical Properties

The study of the presence of acidic or basic functional groups on the surface adsorbents very important, which these groups effect to the surface charge of the adsorbent and adsorption solution. The amounts of acidic and basic surface groups were determined by Boehm's method (Boehm's titration) [34]. Dried adsorbents of 0.075 g were placed in four Erlenmeyer flasks added to each 25 mL of following 0.05 N aqueous solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate and hydrochloric acid. The

samples were shaken for 72 hr at 25°C .

The equilibrated solutions were filtered to remove adsorbent particles, 5 mL were taken off and then titrated with 0.05 HCl or NaOH. The pH of the point of zero charge pH_{PZC} and the pH surface was calculated for each adsorbent by using an acid-base titration method [35]. The results of Behom's titration and pH determination present in Table 3. The amounts of acidic and basic total surface groups, expressed in meq/g, SZC-AC prepared with H_2SO_4 present a higher number of acidic functions than SZC adsorbent.

Table 3. The chemical characteristics of SZC and SZC-AC adsorbents.

Adsorbents	Surface groups (meq/g)					Surface charge	
	Carboxyls	Lactones	Phenols	Acidic	Basic	Surfaces pH	pH_{PZC}
SZC	1.2	6.00	9.65	16.85	4.54	6.25	6
SZC-AC	2.93	23.2	13.17	39.3	4.20	4.65	3.2

3.3.1. The Effect of the Initial Concentration

The adsorption is greatly influenced by the concentration of the solution and adsorption reaction are directly proportional to the concentration of the solution [36]. A concentration range of MG 5 to 85 mg/L onto ZSC and 80 to 550 mg/L onto ZSC-AC. Figure 6 shows the effect of initial MG concentration on the adsorption capacity of SZC and SZC-AC. We were found that with the increase in concentration of the MG from 5 to 60 mg/L, the adsorption capacity of MG adsorbed increased sharply from 4.662 to 45.625 mg/g adsorption for SZC, the adsorption capacity

increased from 49.470 to 365.251 mg/g when initial concentration of MG increasing from 50-450 mg/L for SZC-AC.

It attributed to an increase MG concentration, the rate of diffusion and therefore the higher the adsorption capacity [37]. At equilibrium enhanced slightly from 48.873 to 49.258 mg/g and from 371.3061 to 373.0871 with an increase in the initial dye concentration increased from 70 to 85 mg/L and from 500 to 550 mg/L onto SZC and SZC-AC, respectively. Due to the saturation of the available binding sites on the adsorbent [38].

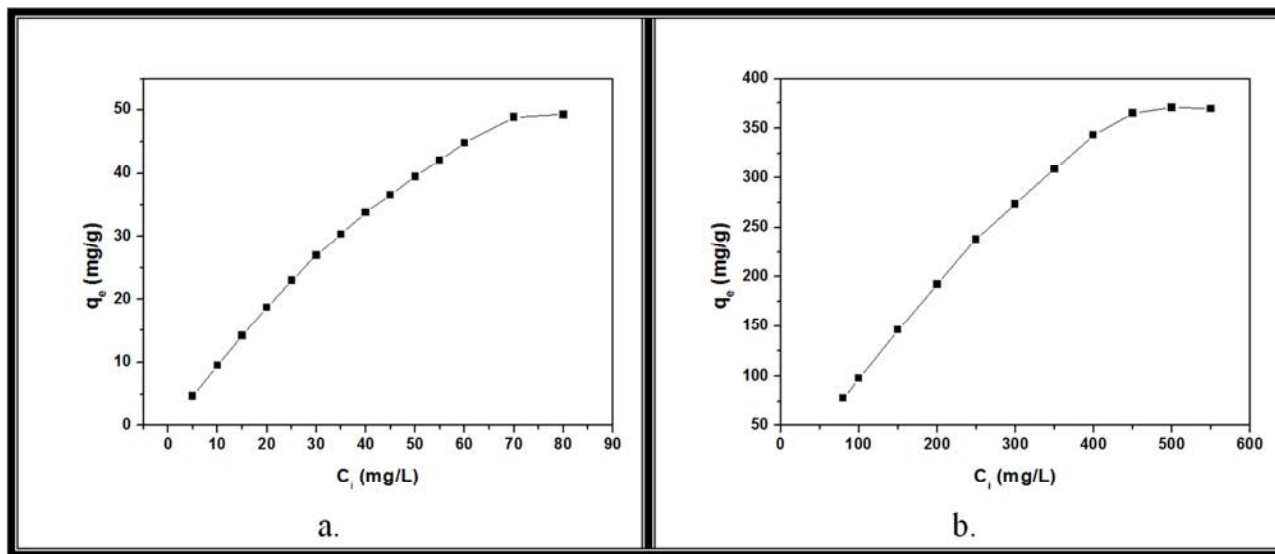


Figure 6. Effect of initial concentration of MG on the adsorption capacity of a. SZC, and b. SZC-AC adsorbent.

3.3.2. Effect of Contact Time on Adsorption

Figure 7 shows the effect of contact time on adsorption capacity for MG at concentration 70 and 450 mg/L on SZC and SZC-AC, respectively. It was clearly observed that the adsorption process of MG dye onto SZC and SZC-AC was

relatively faster rapidly at the initial time, while with the increase of contact time from 300-480 min, the adsorption of MG increased slowly and gradually tended to equilibrium. Therefore, 360 min was selected as the optimum contact time for all further experiments.

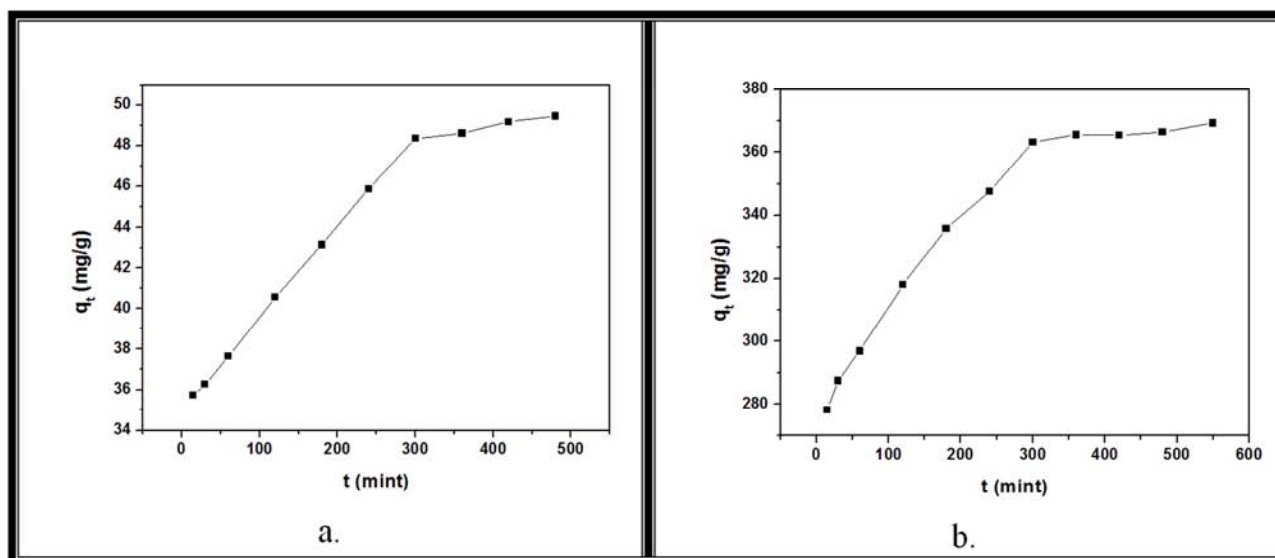


Figure 7. Effect of contact time for adsorption of MG onto a. SZC, and b. SZC-AC, Conditions: C_i SZC = 70 mg/L; C_i SZC-AC = 450 mg/L, $T = 25^\circ\text{C}$.

3.3.3. Effect of pH

The effect of pH was investigated on the adsorption of MG onto SZC and SZC-AC at the pH range 2.00-9.00, the initial dyes concentration 35 mg/L and 200 mg/L onto SZC and SZC-AC, respectively, while the effect of initial pH on the removal percentage of MG, Figure 8. The results show that the removal percentage of MG on SZC and SZC-AC increased very sharply with an increase in pH from 2.00 to 3.00 but when the pH was between 5.00 and 9.00 for SZC and between 3.00 and 9.00. The increment speed of removal percentage was relatively laggardly. When the pH was between 6.00 and 7.00 the removal percentage reaches its maximum value. As shown previously, the pH_{PZC} of SZC and SZC-AC was 6 and 3.2, respectively. The adsorbents surface has a positively charged at pH less than the pH_{PZC} when pH is greater than pH_{PZC} the surfaces of adsorbents have a negatively charged, the negatively charged SZC and SZC-AC surface is favorable for the adsorption of cationic MG dye. Thus, less adsorption of basic MG dye occurs at lower pH [39].

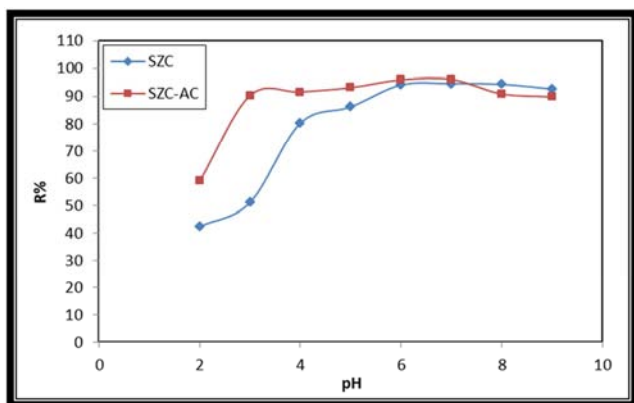


Figure 8. Effect of pH on removal% of MG by SZC, Conditions: C_i SZC = 35 mg/L; C_i SZC-AC = 200 mg/L; 25°C; equilibrium time = 6 hr.

3.3.4. Effect of Adsorbent Dose

The effect of mass dosage was studied for removal of MG on SZC and SZC-AC by agitating in the range of 0.025–0.1375 g, the effect of adsorbent dosage on the removal of MG is shown in Figure 9. It is apparent that increasing the

adsorbent dose from 0.025 to 0.100 g, the percent dye removal increasing readily from 53.257% to 97.802% and from 71.958% to 99.866% onto SZC and SZC-AC, respectively. Results the number of available adsorption sites increases by increasing the adsorbent dose, and slightly enhanced from 97.802% to 98.447% and from 99.866% to 99.940% when adsorbent dose increasing from 0.100 to 0.1375 g due to the number of sites available for adsorption site increases by increasing the adsorbent dose [40].

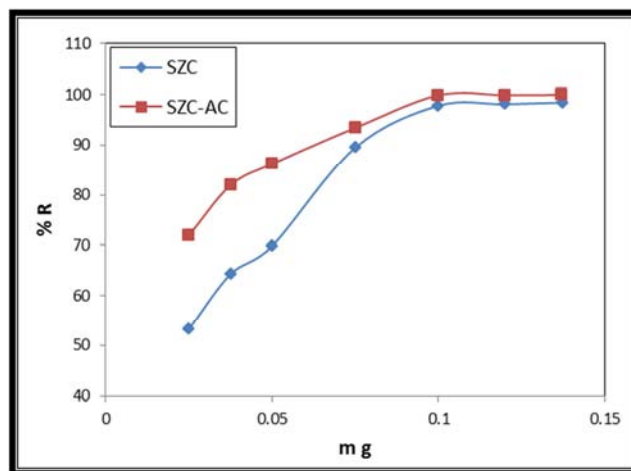


Figure 9. Effect of adsorbent dosage of SZC and SZC-AC on MG removal%. Conditions: $m = 0.025-0.1375$ g; C_i SZC = 70 mg/L; C_i SZC-AC = 450 mg/L; $T = 25^\circ\text{C}$; equilibrium time = 6 hr.

3.3.5. Effects of Interfering Ions

The present of some ions in water samples, which interfere with the removal of MG dye, 200 mg/L of foreign ions such as Acetate, Oxalate, NO_3^- , Cl^- , Na^+ , K^+ , Mg^{+2} , Ca^{+2} , Ba^{+2} , Fe^{+3} in 10 mg/L of MG studies to verify the possibility of analytical applications for the proposed method. The results presented in Table 4 show that these ions did not significantly interfere with the determination of the analysis, especially Mg^{+2} and Fe^{+3} .

Table 4. Effect of interferences on the removal % of MG 10 ppm onto SZC and SZC-AC.

Removal %	Interfering ions									
	Acetate	Oxalate	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Ba^{2+}	Mg^{2+}	Fe^{3+}
SZC	95.870	95.377	82.831	91.740	96.727	97.377	92.442	92.961	88.468	78.494
SZC-AC	97.335	96.332	96.148	96.544	97.335	95.963	92.665	91.557	87.467	82.216

3.3.6. Effect of Ionic Strength

The wastewater contains many ions, therefore the presence of salt in water that may affect the efficiency of the adsorption process. The effects of ion strength on MG adsorbed on SZC and SZC-AC were tested by the addition of NaCl and NaNO_3 to the dye solutions. The concentration of

salts used ranged from 0 to 0.100 mol/L. Figure 10, shows the effect of concentration of salts NaNO_3 and NaCl on the removal MG on SZC and SZC-AC. As can be shown, a rise in salts concentration mol/L decrease in the metal removal%. So, the change of salts concentration, had a major effect on the MG adsorption.

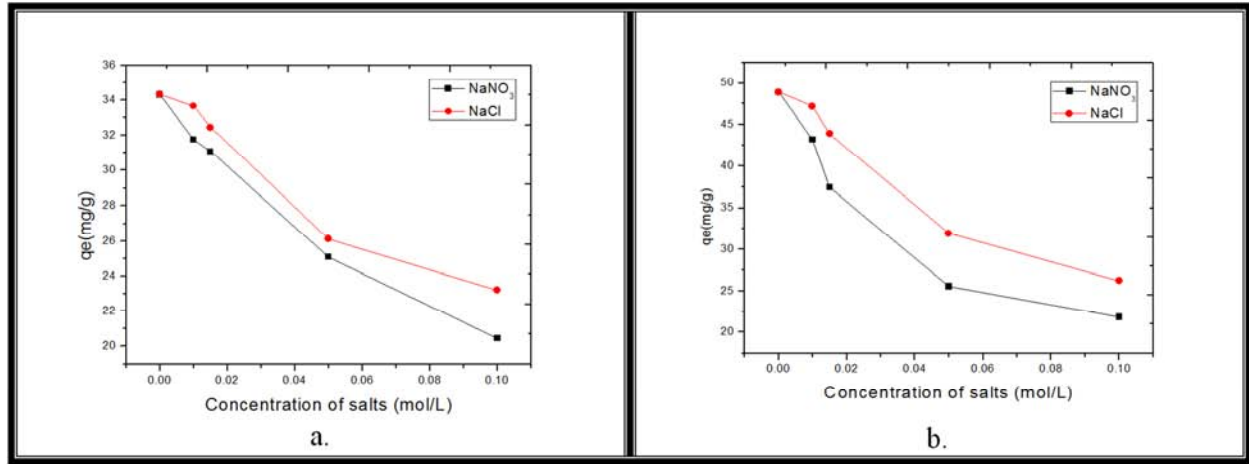


Figure 10. Effect of ionic strength on the removal % of a. MG by SZC, and b. MG by SZC-AC, Conditions: C_i SZC = 70 mg/L; C_i SZC-AC = 400 mg/L; $T = 25^\circ\text{C}$; equilibrium time = 6 hr.

3.3.7. Effect of Temperature on the Adsorption Rate

The influence of temperature on adsorption of MG onto SZC was investigated at 25, 32 and 40°C . The capacities of adsorption of MG were represented in Table 5 and Figure 11a. It can be clearly seen that the amount of MG adsorbed on SZC at equilibrium increases with increasing temperature. When the temperature increased from 25°C to 40°C , the maximum amounts of MG removed increased from 48.873 mg/g to 62.029 mg/g, which indicates a high temperature favors MG adsorption for SZC adsorbents.

It is common that the increasing temperature may create a swelling influence inside the adsorbent structure facilitating [22]. For the SZC-AC, it was observed that the adsorption

capacities decreased as the temperature increased in range 25 – 50°C , which indicates a low temperature favors for removal of MG onto SZC-AC. The experimental results are shown in Figure 11b indicates that the adsorption of MG on to SZC-AC was exothermic in nature.

Table 5. Effect of temperature on maximum adsorption capacities of MG onto SZC and SZC-AC.

q_{\max} mg/g					
SZC			SZC-AC		
25°C	32°C	40°C	25°C	32°C	40°C
48.873	55.047	62.029	370.778	347.256	325.528

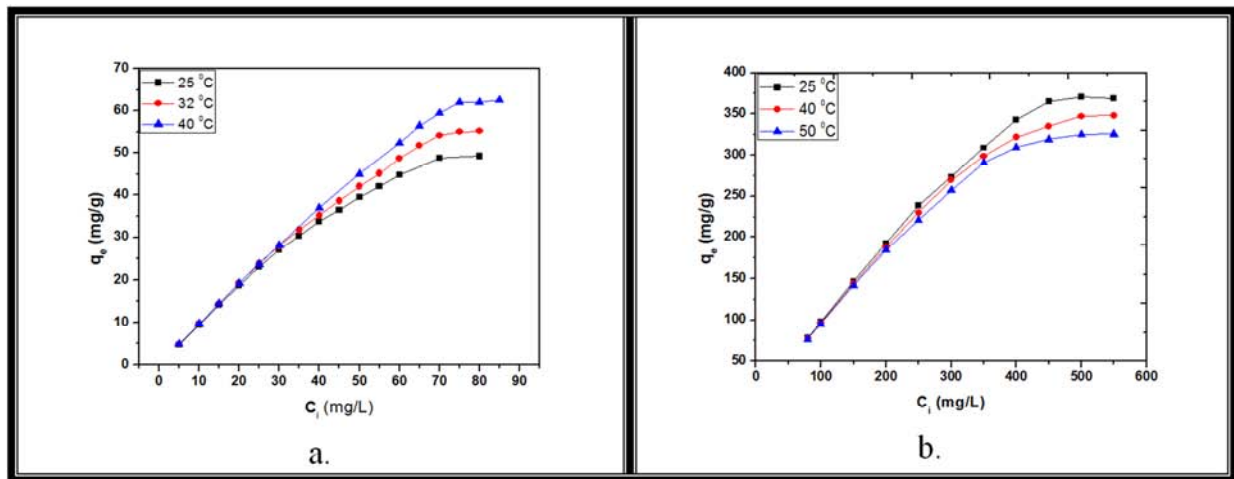


Figure 11. Effect of temperature on maximum capacities of MG onto a. SZC and b. SZC-AC.

3.4. Thermodynamic Studies

The mechanism of adsorption may be determined through other thermodynamic Parameter, such as a change in free energy ΔG° , change in enthalpy of adsorption ΔH° and change in entropy ΔS° . The ΔG° , ΔH° and ΔS° were calculated using the equations (4) – (6):

$$\Delta G^\circ = -RT \ln K_c \quad (4)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

Where R is gas constant (8.314 J/mol/K), T is the absolute temperature in $^\circ\text{K}$ and K is the Langmuir constant. Standard enthalpy ΔH° and entropy ΔS° of adsorption could be estimated from Van't Hoff equation (6).

$$\ln K_c = (\Delta S^\circ/R) - (\Delta H^\circ/RT) \quad (6)$$

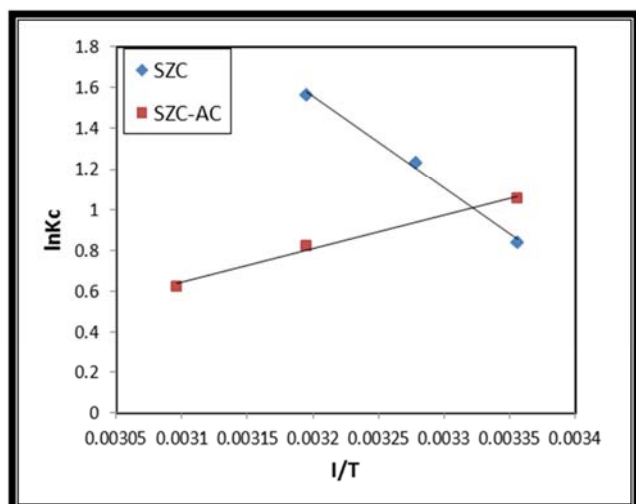


Figure 12. Plots of $\ln K_c$ versus $1/T$ for estimations of thermodynamic parameters of the adsorption process.

Table 6. Thermodynamic functions ΔG° , ΔS° and ΔH° of MG on SZC at (298, 305 and 313°K) and SZC-AC at (298, 313 and 323°K).

SZC					SZC-AC				
ΔH° (KJ/mol)	ΔS° (KJ/mol)	ΔG° (KJ/mol)			ΔH° (KJ/mol)	ΔS° (KJ/mol)	ΔG° (KJ/mol)		
		298°K	305°K	313°K			298°K	313°K	323°K
0.5422	0.0022	-0.031	-0.173	-0.452	-0.044	-0.059	-0.038	-0.031	-0.027

3.4.1. Adsorption Isotherms

In the present study, the equilibrium data were analyzed using both the Langmuir and Freundlich isotherm models at different temperatures. The adsorption isotherm indicates how the adsorption molecules are distributed between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state, the parameters of equilibrium isotherms often give information on adsorption mechanism, surface properties and affinity of the adsorbent [15, 42].

3.4.2. Freundlich Isotherm

The Freundlich adsorption isotherm [43]. Assumes that adsorption occurs on a heterogeneous surface through a multilayer adsorption mechanism and that the adsorbed

Figure 12 was plotted between $\ln K_c$ versus $1/T$, the thermodynamic parameters are presented in Table 6. The positive value of ΔH° suggested the adsorption of MG dye onto SZC is endothermic nature and favored at a high temperature of the adsorption process, but the adsorption of MG dye onto SZC-AC is exothermic in nature. The low value of ΔH° indicates that a weak attractive force between MG and adsorbent surface, this implies the adsorption is physical in nature and loose bonding between the MG molecules and SZC and SZC-AC surface.

The negative values of ΔG° at various temperatures indicate that the adsorption of MG dye onto SZC and SZC-AC is feasible and spontaneous. As shown, the magnitudes of ΔG° from -0.027 to -0.173 K J/mol, a values suggest that the adsorption of MG on SZC and SZC-AC is consistent with electrostatic interaction between adsorption sites and the adsorbing ion physical adsorption, the positive value of ΔS° indicates the increased randomness during the adsorption process [37].

amount increases with the concentration. The Freundlich isotherm is expressed to equation (7):

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (7)$$

Where: n and K_F [mg/g (L/mg)] are both the Freundlich constants giving an indication of adsorption intensity and capacity, respectively.

The degree of non-linearity between solution concentration and adsorption is n dependent as follows: if the value of n is equal to unity, the adsorption is linear; If the value is below to unity, this implies that adsorption processes chemical; if the value is above unity adsorption is a favorable physical process Plot $\ln q_e$ vs $\ln C_e$ Intercept $\ln K_F$ and slop $1/n$, Figure 13.

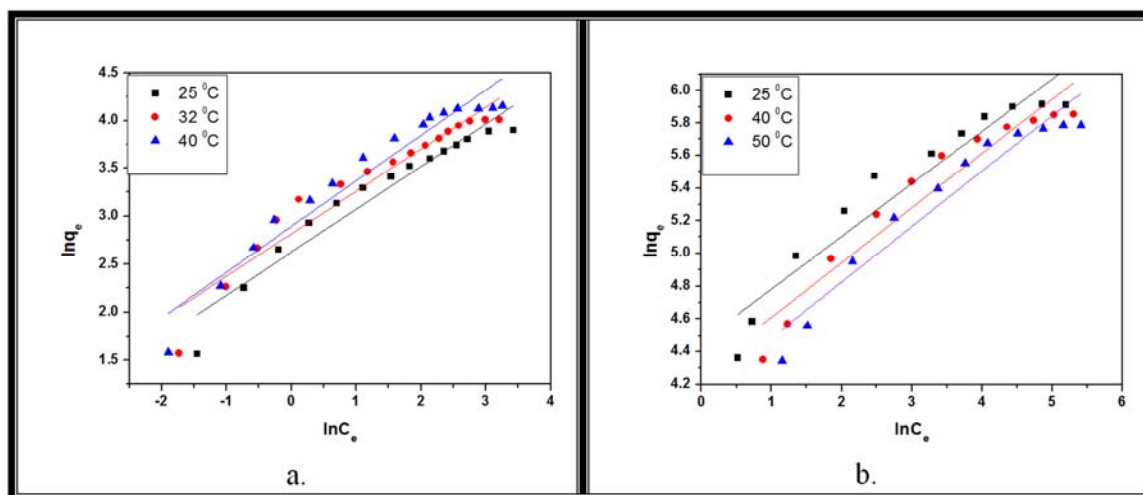


Figure 13. Freundlich plot for adsorption of MG on a. SZC and b. SZC-AC at difference temperature.

3.4.3. Langmuir Isotherm

The Langmuir adsorption model [44] is based on the assumption that a maximum limiting uptake exists, corresponding to a saturated monolayer of adsorbate molecules at the adsorbent surface. The linear form of the Langmuir isotherm equation is given as equation (8):

$$1/q_e = 1/q_{\max} + 1/(q_{\max} K_L C_e) \quad (8)$$

Where C_e : is the concentration of dye at equilibrium in solution mg/L, q_e : is unit equilibrium adsorption capacity, q_{\max} : is the theoretical maximum adsorption capacity mg/g when monolayer is complete, K_L : is the Langmuir adsorption constant i a denoted the energy of adsorption and affinity of the binding sites L/mg.

Both q_{\max} and K_L were a determination from slop and intercept of the plot of $1/q_e$ vs $1/C_e$. Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L is calculated using the following equation (9):

$$R_L = 1/(1 + K_L C_0) \quad (9)$$

Where C_0 : is the initial dye concentration, K_L is Langmuir constant, the value of factor R_L indicates either the adsorption isotherm to be unfavorable $R_L < 1$, favorable ($0 <$

$R_L > 1$), linear ($R_L = 1$), irreversible ($R_L = 0$).

The isotherm parameters for the adsorption of MG by SZC and SZC-AC at different temperatures are given in Table 7. The correlation coefficient (R^2) in the Langmuir model was closer to unity than the Freundlich and theoretical maximum adsorption capacity of adsorbent calculated from Langmuir isotherm equation close to experimental maximum adsorption capacity, this shows the Langmuir model can well describe the adsorption MG dye onto SZC and SZC-AC rather than Freundlich model.

Therefore, it can infer that the mechanism MG adsorption on SZC and SZC-AC is intended to monolayer adsorption. When the temperatures increase, the values k_L calculated from Langmuir model also decrease for adsorption of MG onto SZC This also indicates that the adsorption process is exothermic in nature, but the value of k_L increasing for adsorption of MG into SZC-AC, this also indicates that the adsorption process is endothermic in nature. The value of R_L for all these studies at all temperature between 0 and 1. Therefore, the adsorption is favorable [45]. The difference of k_L values between SZC and SZC-AC refer to the difference in binding strength and capacity of the MG with the surface of the adsorbent [25], Figure 14.

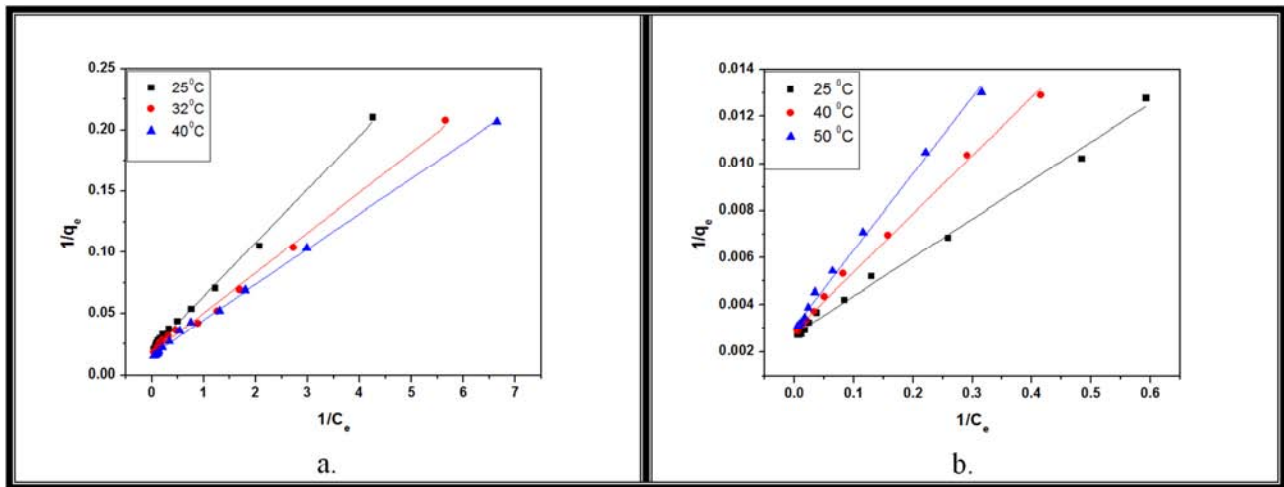


Figure 14. Langmuir plot for adsorption of MG on a. SZC and b. SZC-AC at different temperature.

Table 7. Adsorption isotherm parameters for the adsorption of MG on SZC and SZC-AC at different temperatures.

Adsorbent	T/°C	Langmuir isotherm				Freundlich isotherm		
		q_{\max} mg/g	K_L L/mg	R_L	R^2	K_F L/g	n	R^2
SZC	25	48.780	0.469	0.02955	0.9974	13.791	2.2375	0.9366
	32	57.143	0.534	0.026077	0.9952	16.712	2.26244	0.9308
	40	62.112	0.559	0.024918	0.9981	18.04196	2.01776	0.9514
SZC-AC	25	370.370	0.166	0.01323	0.9981	73.936	2.7655	0.9128
	40	344.828	0.117	0.01865	0.996	71.887	2.9913	0.9281
	50	322.5806	0.095	0.018649	0.996	63.1871	2.94550	0.9338

3.4.4. Adsorption Kinetics

Several mathematical models have been suggested to describe adsorption operations. In this study, for kinetic

models have been applied for the experimental data to understand the rate and can be concluded the mechanism of adsorption, which is the first-order, pseudo-second-order, intra-particle diffusion and Boyd. The linear form of Pseudo-

first-order model [15, 46] is represented by the following equation (10):

$$\ln (q_e - q_t) = \ln q_e - K_1 t \quad (10)$$

Where q_e and q_t refer to the amount of day adsorbent mg/g at equilibrium and at any time, t min and K_1 is the equilibrium rate constant of pseudo-first-order adsorption 1/min. q_e which were obtained from the slopes and intercept of the linear plots in Figure 15a of $\ln(q_e - q_t)$ vs t , the Pseudo-second-order [47]. The equation is represented as equation (11):

$$t/q_t = 1/k_2 q_2^2 + 1/q_2 t \quad (11)$$

In the above equation, q_t denote the amounts adsorbed at equilibrium at any time, q_2 is the maximum adsorption capacity of pseudo-second-order adsorption $\text{mg/g} \cdot \text{min}^{-1}$, the value of k_2 and q_2 for the adsorption of the pseudo-second-order kinetic model can be calculated from the plot of t/q_t against t , Figure 15b.

Kinetic parameters of kinetic models are given in Table 8. Lower values of the correlation value for the pseudo-first-order model, this value suggested that first-order kinetics was not followed during the adsorption process, but the correlation coefficient values of pseudo-second order are closer to unity. Moreover, the q_e values calculated 51.020 mg/g and 370.370 mg/g onto SZC and SZC-AC, respectively. From pseudo-second-order model were more consistent with the experimental values 48.598 mg/g and 365.488 mg/g onto SZC and SZC-AC, respectively.

Therefore, it can be concluded that the adsorption of MG onto SZC and SZC-AC followed pseudo-second-order kinetic model. The adsorption process controlled either by one or more steps, *e.g.* film or external diffusion, pore diffusion, and intra-particle transport surface diffusion and adsorption on the pore surface. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model [48], can be expressed as follows equation (12):

$$q_t = K_i t^{1/2} + c \quad (12)$$

Where q_t is the amount of solute on the surface of adsorbent at time t (mg/g) K_i is the intra-particle diffusion rate constant $\text{mg}/(\text{g} \cdot \text{min}^{1/2})$, and c is a constant reference to the thickness of the boundary layer, the larger value of c , the greater the boundary layer effect.

Figure 15c presents the plots of q_t of MG onto SZC and SZC-AC versus $t^{1/2}$ for adsorbents revealed that the data points are related by two straight lines, then the adsorption process controlled by more steps, the first straight portion represents to mass transfer MG from bulk solution to the external surface of adsorbents and diffusion of MG onto the adsorption site. The straight line deviation from the origin indicates that the adsorption process is not only controlled by intra-particle diffusion and might be due to the difference in the mass transfer rate in the initial and final stages of adsorption, the large value of the intra-particle diffusion constant C_{int} that indicate the boundary layer has a more significant effect about the diffusion mechanism [49].

3.4.5. The Boyd Kinetics Model

To suggest the slow step involved in the adsorption process the kinetics data were also subjected to Boyd kinetics [50], the Boyd kinetics model is represented by the following equation (13):

$$Bt = -0.4977 - \ln(1-F) \quad (13)$$

Where F represents the fraction of solute adsorbed at any time, t min, as calculated from equation (14):

$$F = q_t/q_0 \quad (14)$$

Where q_0 is the amount of adsorbents adsorbed at infinite time mg/g and q_t is the amount of adsorbents adsorbed at any time t min. Bt calculated from equation (13) and the Bt values were plotted vs time t , Figure 15d, when the line pass throw the origin, the adsorption mechanism was governed by external mass transport where particle diffusion is the rate-limiting step.

Table 8. Kinetic parameters for the adsorption MG onto ZSC and ZSC-AC.

	Kinetic parameter	SZC	SZC-AC
Model	$q_{e,exp}$ (mg/g)	48.599	365.491
	q_{e1} (mg/g)	25.557	152.536
	K_1 (min^{-1})	0.002	0.012
	R^2_1	0.905	0.933
Pseudo first-order	q_{e2} (mg/g)	51.020	370.370
	K_2 (mg/g min)	0.0256	0.0036
	R^2_2	0.9975	0.9989
	C	31.766	125.650
Pseudo second-order	K_{int} (mg/g.min ^{1/2})	0.8636	6.272
	R^2	0.9764	0.995
	intercept	1.314	5.027
Boyd	R^2	0.9499	0.933

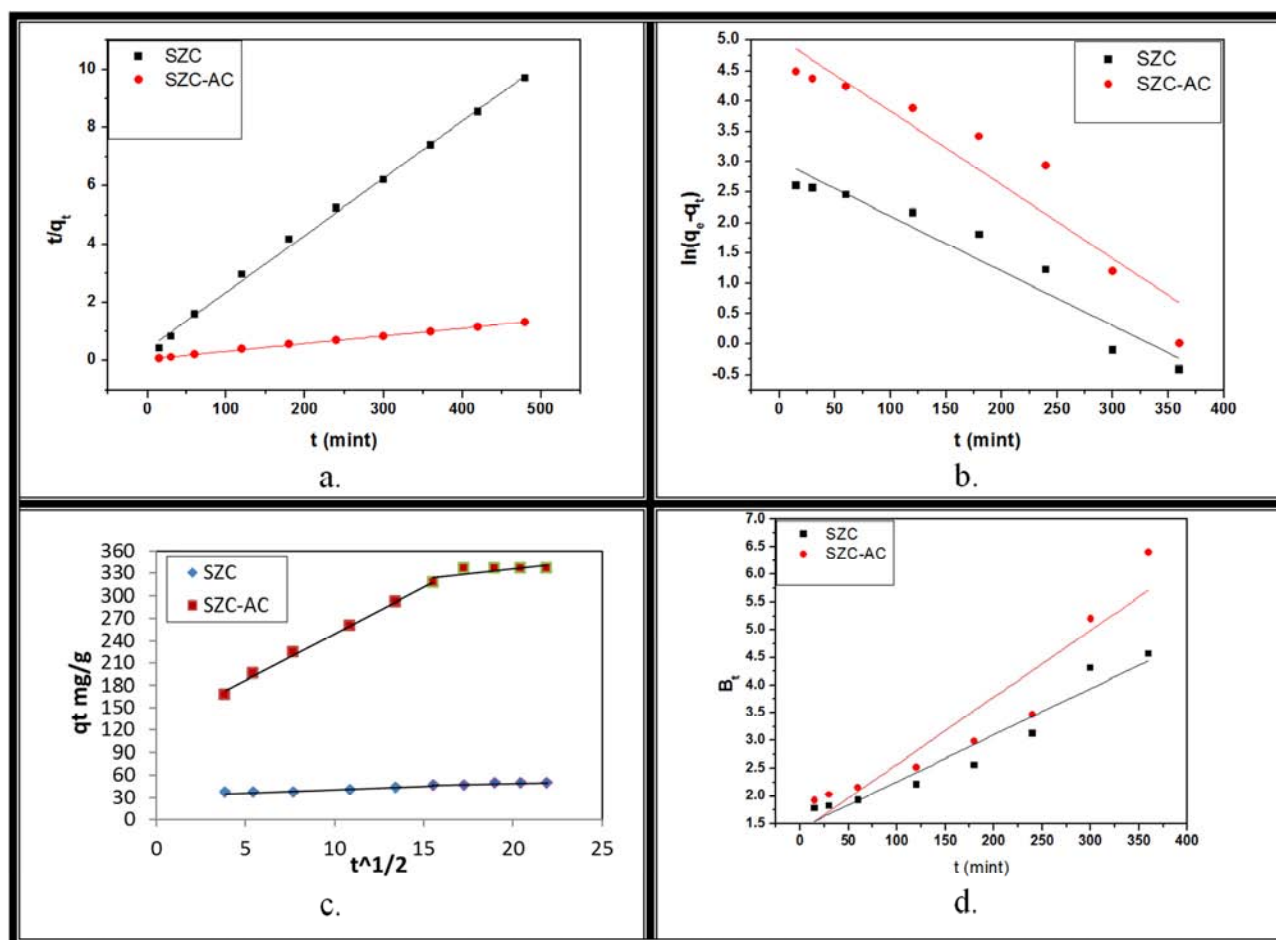


Figure 15. Kinetic models for adsorption of MG a. Pseudo-first order; b. Pseudo-second order; c. Intra-particle diffusion, and d. Boyd model.

3.5. Analytical Applications

To verify the possibility of analytical applications for the prepared adsorbents. For this purpose, known amounts MG spiked to different natural water samples as tap water, sea water and wastewater. The results were listed in Table 9, the recovery % ranged between 94.737% and 99.7691% with a relative standard deviation (RSD %, < 3), the obtained results indicated the prepared adsorbents were successfully, feasible and satisfactory to analyze water samples, Table 10.

Table 9. Recovery% and RSD% of MG from different water samples using SZC and SZC-AC, $n = 3$.

Sample Location	Adsorbate	MG added (mg/g)	R%	RSD%
Tap water from the lab	SZC	2	95.1715	0.739
		4	94.9285	0.553
		8	94.7372	0.796
	SZC-AC	5	98.7327	0.488
		10	98.5447	0.685
		15	98.2221	0.906
Sea water Mukalla city	SZC	2	97.2616	0.505
		4	96.3231	0.539
		8	96.2464	1.293
	SZC-AC	5	99.7691	0.167
		10	99.2507	0.443
		15	99.190	0.436
Wastewater Al-Khor – Mukalla city	SZC	2	96.467	0.621
		4	96.547	0.610
		8	96.047	0.450
	SZC-AC	5	99.220	0.296
		10	99.301	0.306
		15	97.194	4.605

Table 10. Adsorption capacities of different adsorbents previously reported for the removal of MG compared with SZC and SZC-AC.

Adsorbents	Adsorption capacity (mg/g)	Reference
Shells seeds of <i>Ziziphus spina christi</i> SZC	48.780	Present study
Modified shells seeds of <i>Ziziphus spina christi</i> with Sulphuric acid SZC-AC	370.370	Present study
Neem sawdust	4.354	Khattari and Singh [51]
Chemically modified rice husk	17.98	Chowdhury <i>et al.</i> [17]
CO ₂ -activated porous carbon CAC from cattail biomass	210.18	Yu <i>et al.</i> [52]
Wheat Bran	66.57	Wang <i>et al.</i> [20]
Cellulose modified with phthalic anhydride CPA	111.00	Akl <i>et al.</i> [41]
Sulphuric acid-treated sawdust PCSDC	65.8	Garg <i>et al.</i> [53]
Orange peel	483.63	Kumar and Porkodi [18]
NaOH- modified breadnut peel	353.00	Chieng <i>et al.</i> [54]
EDTAD-modified Sugarcane Bagasse	156.20	Xing and Deng [55]
phosphoric acid esterifying soybean hull	178.57	Gong <i>et al.</i> [56]
Modified rice straw MRC with citric acid AC	256.41	Gong <i>et al.</i> [40]

4. Conclusions

From this work, it is seen that SZC and SZC-AC could be a good adsorbent for removal the cationic dye from water. The pH of the adsorption system did not present significant effects on the adsorption capacity for values below the PZC and the adsorption process performed without controlling the pH of the medium. Thermodynamic parameters suggest that the adsorption is a physical process, spontaneous, and exothermic on SZC and exothermic in nature. The experimental data were well fitted to the Langmuir isotherm model at all temperature and monolayer adsorption capacity increasing after modify. The kinetics of MG adsorption was based on the assumption of the pseudo-second-order mechanism. The results presented in this study indicate that Shell's Seeds of *Ziziphus spina christi* presents great potential as an inexpensive and easily available alternative adsorbent for the removal of cationic dyes in wastewater treatments.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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