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Kinetics and Thermodynamics of Activated Sunflowers Seeds Shell Carbon (SSSC) as Sorbent Material

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Abstract

Carbon prepared from waste plants for the treatment of dyeing industry effluents has high significance in environmental sustainability and economic viability. Methylene Blue (MB) in aqueous solutions was subjected to color removal by the adsorption technique onto activated sunflowers seeds shell carbon (SSSC) as agricultural material. Results obtained indicate that the removal efficiency of Methylene Blue varies from 92.7 to 95.6% by rising the temperature from 30 to 60°C at pH from 6 to 8. The results fit the BET model for adsorption of Methylene Blue on SSSC, verify the assumption that the adsorbate molecules could be adsorbed in more one layer thick and non homogenous on the surface of the adsorbent. A comparison of kinetic models (pseudo first-order, the pseudo second-order, Elovich and intraparticle diffusion) at different conditions showed that the pseudo second-order kinetic model correlate the experimental data well. Van't Hoff equation was used to evaluate the thermodynamic parameters (ΔH, ΔS, and ΔG), which indicate that adsorption processes for the present work are exothermic, and this is agreement with the stability of adsorption capacity with temperature, chemically in nature, and spontaneous.

Keywords: Adsorption; Isotherms; Kinetic models; Thermodynamics; Sunflowers seeds shell

Nomenclature

A: Constant describing the energy of interaction between solute and adsorbent surface;

C: Initial concentration (mg/l);

C_e: Concentration equilibrium (mg/l);

C_s: Saturation concentration of solute (mg/l);

K_F &n: Freundlich constants;

m: Weight of adsorbent (mg);

k_1: Rate constant of pseudo first-order adsorption (l/min);

k_2: Rate constant of pseudo second-order adsorption (g/mg. min);

K_D: Distribution coefficient (cm³.g⁻¹);

k_{id}: Intraparticle diffusion rate constant (min⁻¹);

K_L: Constant related to the adsorption/desorption energy (l g⁻¹);

q_e: Adsorption capacity at equilibrium, (mg of dye/g adsorbate);

q_{max}: Maximum sorption (mg of dye/g adsorbate);

q_t: Adsorption capacity at time t, (mg of dye/g adsorbate);

R: universal gas constant (j/mole. K);

R: Percent (MB) adsorbed;

t: Contact time (min);

V: Volume of the solution;

x: Amount of solute adsorbed (mg);

X_m: Amount of solute adsorbed in forming a complete mono layer (mg of dye/g adsorbate);

α: Initial adsorption rate (mg of dye/g adsorbate. min);

β: Desorption constant (g/mg) during any experiment;

Introduction

The hulls, or shells, of Sunflower Seed are mostly composed of cellulose. They decompose slowly. They are sometimes burned as biomass fuel. Sunflower seeds are more commonly eaten as a healthy snack than as part of a meal. They can also be used as garnishes or ingredients in various recipes. The seeds may be sold as in-shell seeds or dehulled kernels [1].

Cationic dyes, such as Methylene Blue (MB), were used initially for dyeing of silk, leather, plastics, paper, and cotton mordant with tannin, as well as for the production of ink and copying paper in the office supplies industry [2]. In the textile sector, an estimated 10-20% of dyes (active substance) used is lost in residual liquors through the exhaustion and washing operations [3]. The releasing of dyes to the environment can cause acute and/or chronic effects on the exposed organisms, adsorb or reflect sunlight entering into water, and thus result in change of food chain [4].

Previous studies found that MB molecules existed as dimer or as aggregates at the surface, as well as a protonated form depending on the concentration and the surface properties [5]. Such extensive use of dyes and pigments often poses problems in the form of colored wastewater that require pre-treatment for color removal prior to disposal into receiving water bodies or publicly owned treatment works [6]. The main problem for dyestuff manufacturers and users is the removal or reducing the quantity of color in effluent and water sources [7].

At the present time there is no single process capable of adequate treatment [8]. Most of the existing processes include adsorption, usually

with activated carbon (AC) [9]. The adsorption of the cationic dye, MB, has been used for a long time for the evaluation of the adsorption properties of AC, and in monitoring the production and quality of AC prepared from coal, in fluidized bed [10,11]. Adsorption from dilute aqueous solutions onto solid surfaces is a highly attractive separation technique for many applications, such as wastewater treatment, liquid mixture separation and purification, or polar organic solutes recovery from biotechnology processes [12,13]. In particular, adsorption provides a technique of great interest to remove dyes from municipal and industrial wastewater [14,15]. This can be achieved by using adsorbents with a high adsorptive capacity and selectivity [16].

The adsorption process can be either physical or chemical in nature, and frequently involves both. Physical adsorption involves the attraction by electrical charge differences between adsorbent and the adsorbate. Chemical adsorption is the product of a reaction between the adsorbent and the adsorbate [17]. In recent years, stringent government regulations have made it mandatory to stop such effluents, unless they are treated properly; hence, the removal of color from the effluent discharge has become environmentally important [18,19].

Materials and Methods

Preparation of (SSSC)

The dried Sunflowers Seeds shells ware soaked in a boiling solution of 10% H_3PO_4 for one hour and kept at room temperature for 24 h. Thereafter, the wood material was separated, air dried at room temperature and carbonized in muffle furnace at 400°C for 20 min. The carbon was ground to powder and activated in a muffle furnace at 800°C for a period of 10 min. Then the activated carbon was washed with plenty of distilled water to remove residual acid, and dried at 105°C. The washed carbon ware lightly ground in a mortar and sieved through 0.5 mm and 0.05 mm diameter by means of a test sieve shaker respectively.

Batch adsorption studies

Batch experiments with SSSC were conducted to investigate the parameters effects of initial adsorbate particle size and concentration, adsorption time, pH, temperature on MB adsorption. All reagents used were of analytical reagent (AR) grade (Sigma-Aldrich, Germany). MB samples were prepared by dissolving a known quantity of the dye in distilled water and used as a stock solution and diluted to the required initial concentration (range: 25 to 125 mg/l). 50 ml of MB solution of known concentration (c_o) was taken in a 100 ml conical flask with the required amount of adsorbent and was shaken for different time intervals in a shaker at different pH values and different temperatures. Then, the solution was filtered through a filter paper. UV-visible spectrophotometer (model PHTOMECH 301-D⁺) was employed to determine the remaining concentrations of MB in the filtrate at 670 nm.

Adsorption Isotherms Study

Equilibrium studies that give the capacity of the adsorbent and adsorbate are described by adsorption isotherms, which is usually the ratio between the quantity adsorbed and that remained in solution at equilibrium at fixed temperature. Freundlich, Langmuir and BET isotherms are the earliest and simplest known relationships describing the adsorption equation [20-28]. Adsorption isotherms have been classified into six characteristic types. Microporous adsorbents produce adsorption isotherms of Type 1 (which has a convex shape) and it is also associated with monomolecular layer adsorption. Types II and III depict adsorption for multi-molecular layer formation while Types IV and V describe the adsorption process of multi-molecular layer formation and condensation in pores. Type VI represents surface phase transition of a monomolecular layer on a homogeneous surface [29].

Langmuir isotherm

The Langmuir equation is used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface and is expressed by:

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

The linearise form of the above equation after rearrangement is given by:

$$C_e / q_e = 1 / q_{max} K_L + C_e / q_{max} \tag{2}$$

The experimental data is then fitted into the above equation for linearization by plotting C_e / q_e against C_e.

Freundlich isotherm

The Freundlich model named after Freundlich (1926) [30] is an empirical equation used to estimate the adsorption intensity of the sorbent towards the adsorbate and is given by:

$$q_e = \frac{K_F C_e}{n} \tag{3}$$

Also, the value of n indicates the affinity of the adsorbate towards the adsorbent. The above equation is conveniently used in linear form as:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \tag{4}$$

A plot of $\ln C_e$ against $\ln q_e$ yielding a straight line indicates the conformation of the Freundlich adsorption isotherm. The constants $1/n$ and $\ln K_F$ can be determined from the slope and intercept, respectively.

BET isotherm

The BET derived an adsorption isotherm based on the assumption that the adsorbate molecules could be adsorbed in more than one layer thick on the surface of the adsorbent [31]. Their equation, assumed that the energy of adsorption holds the first monolayer but that the condensation energy of the adsorbate is responsible for adsorption of successive layers. The equation, known as the BET equation, is commonly written as follow:

$$\frac{x}{m} = \frac{A C X_m}{(C_s - C)\left(1 + \frac{(A-1)C_s}{C}\right)} \tag{5}$$

or

$$\frac{C}{(C_s - C)\left(\frac{x}{m}\right)} = \frac{1}{A X_m} + \frac{(A-1)}{A X_m}\left(\frac{C}{C_s}\right) \tag{6}$$

Thus, plotting $[C/(C_s-C)]/(x/m)$ against C/C_s will give rise to straight lines with slope $(A-1)/AX_m$ and intercept $1/AX_m$ for adsorption processes that conform BET equation [23].

Adsorption Dynamics Study

The study of adsorption dynamics describes the solute uptake rate

and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. Kinetics of MB adsorption on the SSSC was analyzed using pseudofirst-order, pseudo second-order, Elovich and intraparticle diffusion kinetic models [32,33].

The pseudo first-order model

The pseudo first-order equation [34] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{7}$$

At $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, the integrated form of Equation (7) becomes:

$$(\log q_e - \log q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{8}$$

where k_1 and q_e can be determined from the slope and intercept of the plot.

The pseudo second-order model

The pseudo second-order kinetic rate equation is expressed as [35]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

At $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, the integrated form of Equation (9) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \tag{10}$$

Equation (4) can be rearranged to obtain Equation (11), which has a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{11}$$

If the initial adsorption rate, h (mg/g. min) is:

$$h = k_2 q_e^2 \tag{12}$$

then Equations (11) and (12) become:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \tag{13}$$

The plot of (t/q_t) and t of Equation (11) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

The Elovich model

The Elovich model equation is generally expressed as:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{14}$$

To simplify the Elovich equation, [36] assumed $\alpha\beta t \gg t$ and by applying the boundary conditions $t=0$ to $t=t$ and $qt=0$ to $q_t=q_t$, Equation (14) becomes:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{15}$$

A plot of q_t vs. $ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) ln(\alpha\beta)$.

The intraparticle diffusion model

The intraparticle diffusion model is expressed as [37]

$$R = k_{id}(t)^a \tag{16}$$

A linearized form of the equation is obtained as:

$$\log R = \log k_{id} + a \log(t) \tag{17}$$

If MB adsorption fits the intraparticle model, a plot of $\log R$ vs. $\log t$ should yield a linear relationship with a slope of a and an intercept of $\log k_{id}$.

Results and Discussion

General information of SSSC

A Cross sections through and Scanning electron micrographs for activated sunflowers seeds shell carbon was shown in Figures 1 and 2 with magnification scale of 500.
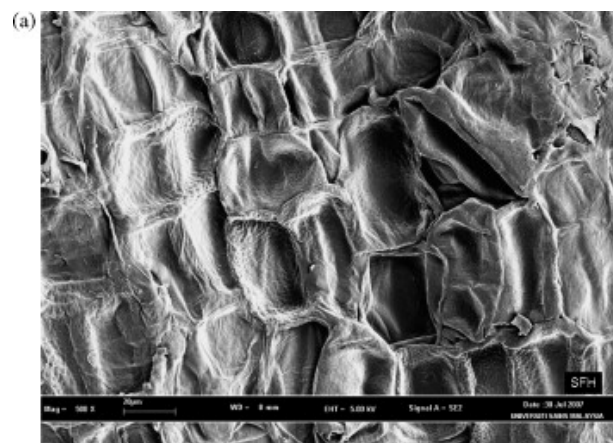

Figure 1: Typical SEM micrograph of SSH particle (magnification: 500): before dye sorption.
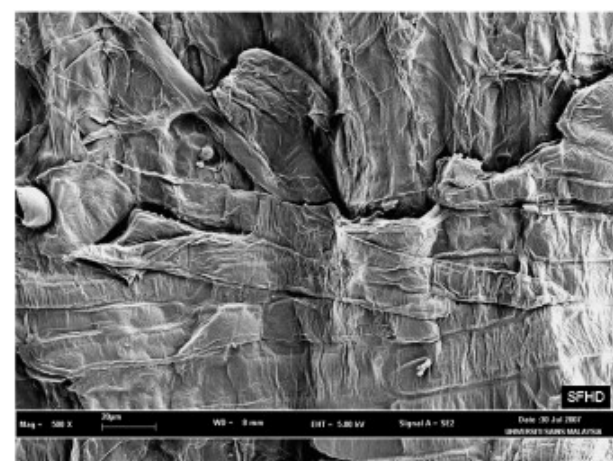

Figure 2: Typical SEM micrograph of SSH particle (magnification: 500): with dye sorbed.
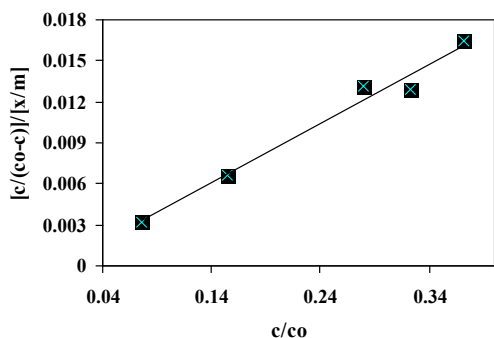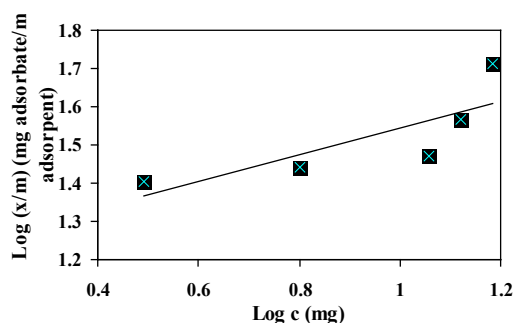
Figure 3: BET isotherm.
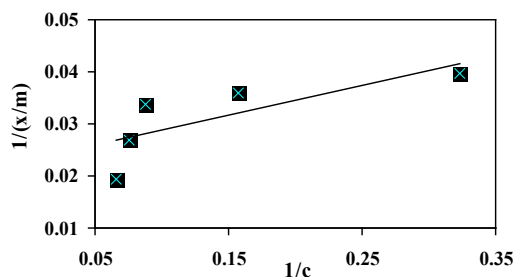

Figure 4: Freundltish isotherm.

Figure 5: Langmuir isotherm.

Adsorption isotherms

The results of this study show that SSSC was effective, in adsorbing MB as its removal reached 95.6% at 60°C and dye initial concentration of 50 mg/l. Adsorption of MB was highly pH-dependent and the results showed that the optimum pH for the removal was found to be 6-8, at which MB exists mostly as the most easily adsorbed form aqueous solution increases as the initial MB concentration. Also increasing temperature, smaller adsorbate particle were found to increase the percentage removal of MB. The Experimental data were applied in the three isotherms (Figures 3-5), which results indicate that the adsorption of MB on SSSC fits the BET model with r^2=0.978, verifying the assumption that the adsorbate molecules could be adsorbed in more than one layer thick on the surface of the adsorbent.

Adsorption dynamics

Effect of adsorbate concentrations: The removal of MB by adsorption on SSSC was found to increase with time and attained a maximum value at 150 min. On changing the initial concentration

of MB solution from 25 to 125 mg/l, the amount adsorbed increased at 30°C, pH 7 and particle size of 0.05 mm. The experimental results correlate with the theoretically predicted curves. Results obtained show good compliance with the pseudo second-order kinetic model (Figure 6), with values of correlation coefficient, $r^2 \cong 0.99$.

Effect of adsorbent particle size: The batch adsorption experiments were carried out using adsorbent with different particle sizes, (blew 0.05 to over 0.5 mm) at pH 7, 30°C, and initial concentration of 25 mg/l. The removal of MB increased with the decrease in particle size. The data obtained separately for each of the kinetic models from the slopes of plots, show a good compliance with the pseudo second-order equation (Figure 7), with values of correlation coefficient, $r^2 \cong 0.99$.

Effect of temperature: Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution.

In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate. The experimental data were obtained at pH 7, particle size blew 0.05 mm, and initial concentration of 25 mg/l. The increasing adsorption rate of MB on the surface of SSSC may be explained by considering more conversion of the dimer species to monomers. The data obtained for each of the kinetic models from the slopes of plots (Figure 8) show a good compliance with the pseudo second-order equation, with values of correlation coefficient, $r^2 > 0.99$.

Effect of adsorbent dose: MB uptake was studied using different doses of SSSC by using 50 ml of solution at pH 7, 30°C, particle size blew
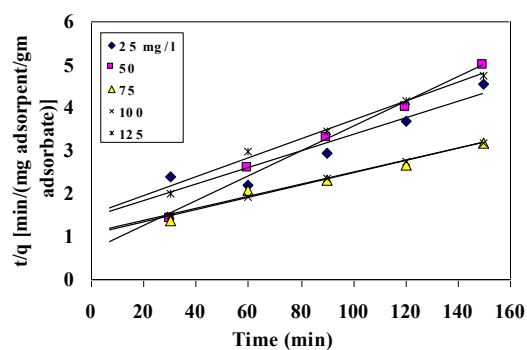

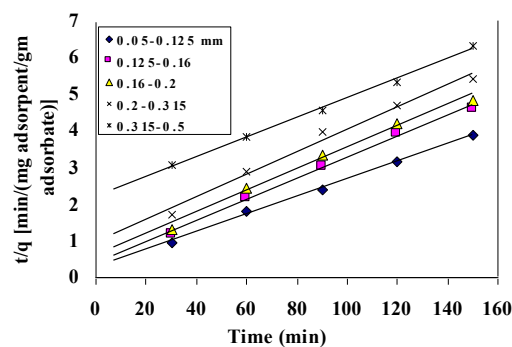**Figure 6**: Pseudo second-order equation at different adsorbate concentrations.

Figure 7: Pseudo second-order equation at different adsorbent particle size.
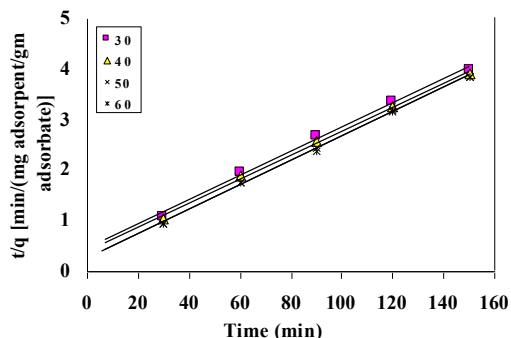
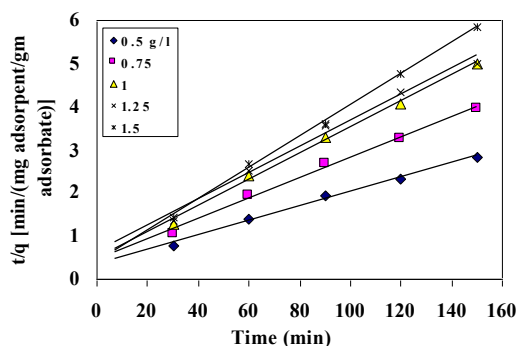**Figure 8**: Pseudo second-order equation at different temperatures.

Figure 9: Pseudo second-order equation at different adsorbent dose.
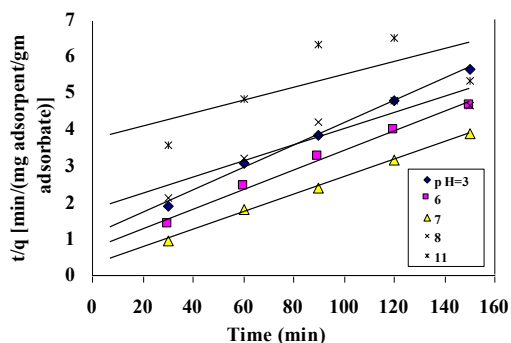

Figure 10: Plot of pseudo second-order equation at different pH values.

0.05 mm and initial concentration of 25 mg/l. The concentrations used were 0.5, 0.75, 1, 1.25 and 1.5 gm adsorbent/ liter adsorbate, keeping the batch experimental volume the same in all cases. The results indicated that the percent adsorption increased with the increase in SSSC dose. The curves (Figure 9), showed good compliance with pseudo second-order model with values of correlation coefficient, $r^2 \cong 0.99$.

Effect of pH: The removal of MB was studied at different pHs in the range 3-11 by SSSC at initial MB concentration of 25 mg/l, and a temperature of 30°C, particle size blew 0.05 mm. The variation in adsorption capacity in this pH range is largely due to the influence of pH on the adsorption characteristics of the SSSC which indicates that the adsorption capacity of the adsorbent is clearly pH dependent. The optimum removal (95%) was observed in the pH range 6-8. Results
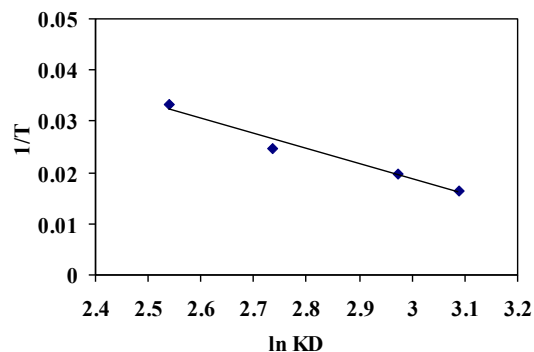

Figure 11: Plot of K_D versus 1/T.

also showed that the adsorption reaction can be approximated with the pseudo second-order kinetic model (Figure 10), with values of correlation coefficient, $r^2 \cong 0.99$. The rate constants and values of correlation coefficient represented in Table 1.

Thermodynamic parameters

Determination of ΔHᵒ, ΔSᵒ and ΔGᵒ: The values of the thermodynamic parameters, enthalpy variation (ΔH) and entropy variation (ΔS), were calculated from the curve relating the distribution coefficient (K_D) as a function of temperature (Figure 9) using the equation:

$$\ln K_D = \left(\frac{\Delta S^\circ}{R}\right) - \left(\frac{\Delta H^\circ}{RT}\right) \tag{18}$$

where K_D is the distribution coefficient (cm³.g⁻¹), defined as:

$$K_D = \frac{Q}{C_e} \tag{19}$$

where Q is the amount adsorbed (mg adsorbate/g adsorbent) described by the equation:

$$Q = \frac{V(C - C_e)}{m} \tag{20}$$

where C and C_e are the initial and equilibrium concentrations of the solute, respectively (mg.cm⁻³). The calculated data for K_D and Q are shown in Table 2.

The free energy change (ΔG^o) parameter was calculated using equation 21:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{21}$$

From Figure 11 the values of ΔH^o, ΔS^o were determined from the slopes and intercepts of the curves, respectively as well as the calculated values of ΔG^o and are listed in Table 3. Investigation of the obtained values of the thermodynamic parameters shows that the adsorption process is exothermic. This is in accordance with increasing adsorption equilibrium with increasing temperature.

Determination of mean free:

I. Energy (E)

The mean free energy of adsorption (E) is the free energy change when one mole of ions is transferred to the surface of the membrane from infinity in the solution and it is calculated from:

$$E = -(2K_D R)^{\frac{1}{2}} \tag{22}$$

Parameter		First order		Second order			Elovich model			Intraparticle diffusion		
		K_1	r^2	q_e	K^2	r^2	β	α	r^2	k_{id}	a	r^2
pH	3	-0.0112	0.954	32.68	0.0009	0.997	0.144	2.13	0.991	12.15	0.3373	0.992
	6	-0.0093	0.922	37.17	0.0010	0.992	0.1508	5.16	0.974	21.93	0.2519	0.988
	7	-0.0119	0.961	41.49	0.0021	0.999	0.2031	90.01	0.947	46.94	0.1414	0.949
	8	-0.0067	0.812	45.05	0.0003	0.975	0.0992	1.19	0.879	6.7	0.4727	0.951
	11	-0.0073	0.722	57.47	0.0001	0.469	0.0954	0.64	0.78	1.94	0.6753	0.912
particle size (mm)	0.05	-0.0119	0.962	41.49	0.0021	0.999	0.2031	90.01	0.947	46.94	0.1414	0.949
	0.125	-0.0062	0.941	34.48	0.0023	0.999	0.2575	95.08	0.967	39.73	0.1344	0.977
	0.16	-0.0084	0.877	34.01	0.0015	0.991	0.2020	14.03	0.943	28.53	0.1882	0.962
	0.2	-0.0092	0.896	32.68	0.001	0.985	0.1616	11.92	0.961	16.27	0.2802	0.983
	0.315	-0.0118	0.977	37.31	0.0003	0.995	0.1123	0.89	0.996	3.65	0.5634	0.982
Adsorbent dose (mg/l)	0.5	-0.0115	0.936	59.52	0.0008	0.995	0.1061	16.68	0.976	22.58	0.2095	0.986
	0.75	-0.0111	0.926	42.37	0.0013	0.994	0.1650	20.12	0.943	22.45	0.2724	0.982
	1	-0.0107	0.949	32.89	0.002	0.996	0.2304	28.55	0.955	32.29	0.1634	0.965
	1.25	-0.0084	0.84	33.01	0.0014	0.986	0.2125	14.41	0.898	35.00	0.1842	0.923
	1.5	-0.0119	0.962	27.70	0.0032	0.999	0.3047	60.01	0.947	46.94	0.1414	0.949
Conc. (mg/l)	25	-0.0138	0.989	51.81	0.0003	0.989	0.0784	1.37	0.906	31.00	0.1872	0.97
	50	-0.0186	0.926	34.84	0.0012	0.991	0.1676	6.38	0.930	23.67	0.2335	0.938
	75	-0.0099	0.977	70.42	0.0002	0.974	0.0605	1.91	0.970	4.93	0.5011	0.983
	100	-0.0114	0.953	71.94	0.0002	0.999	0.0587	1.80	0.998	3.88	0.5384	0.991
	125	-0.0051	0.996	45.05	0.0003	0.987	0.095	1.355	0.983	2.89	0.4759	0.993
Temp. (°C)	30	-0.0084	0.941	42.02	0.0013	0.996	0.1615	17.44	0.980	35.343	0.1902	0.989
	40	-0.0095	0.951	42.37	0.0014	0.997	0.1669	23.51	0.986	38.09	0.1793	0.992
	50	-0.0125	0.919	41.67	0.002	0.999	0.213	127.24	0.975	48.85	0.1336	0.977
	60	-0.0124	0.907	41.84	0.0022	0.999	0.2145	141.32	0.953	49.63	0.1317	0.955

Table 1: The adsorption kinetic model rate constants.

Temperature (°C)	Q	K_D
30	38	12.67
40	38.5	15.4
50	39	19.5
60	39.4	21.89

Table 2: Q and K_D parameters at different temperatures.

ΔH kcal/mol	ΔS kcal/ mol. K.	ΔG (kcal/mol)			
		30°C	40°C	50°C	60°C
-0.058	0.211	-64.1	-66.2	-68.36	-70.45

Table 3: Thermodynamic parameters at different temperatures.

Temperature (°C)	K_D	E, kj/mol
30	12.67	7.08
40	15.4	7.81
50	19.5	8.88
60	21.89	9.31

Table 4: Free Energy (E) at different temperatures.

The mean free energies (*E*) were calculated and documented in Table 4.

The magnitude of E is useful for estimating the type of sorption reaction, since $E < 8$ kJ. mol^{-1}, physical forces such as diffusion processes may affect the sorption mechanism [24]. So, the adsorption of dyes seems to be a complex phenomenon, where diffusion and chemical bonding occur at different temperature ranges, this may support that the monolayer capacity (q_{max}) increases with increasing temperature. But in our work the results indicate a rapprochement of the activation energy with 8 which indicate small influence of the adsorption with temperature increasing. Table 5 shows some of the adsorption capacities of low-cost adsorbents reported in the literature.

Sorbent	q_{max} (mg g^{-1})
Degreased coffee bean	55.3
Treated sawdust	65.8
Arundo donax root carbon	8.69
Activated charcoal	0.179
Waste apricot	116.27
Activated carbons commercial grade	8.27
Laboratory grade activated carbons	42.18
Bentonite	7.72
Sugarcane dust	4.88
Hen feathers	26.1
Iron humate	19.2
Rubber wood sawdust	36.45
Cellulose	2.422
Neem leaf powder	133.6
Ricinus communis	27.78
Lemon peel	51.73
Caulerpa racemosa var. cylindracea	26.57
Rattan sawdust	62.7
Maize cob powder	37.037
Sea shell powder	42.33
Salix Leafs powder	62.35
activated sunflowers seeds shell carbon, (present work)	39.4

Table 5: Comparison between adsorption capacity of low-cost adsorbents.

Conclusion

- Sunflowers Seeds shells Carbon (SSSC) could be used as an alternative low cost adsorbent of dyes from industrial wastewater discharged from dying units.

- The adsorption process fits the BET model, corroborating the

assumption that the adsorbate molecules could be adsorbed in more than one layer thick on the surface of the adsorbent.

• The kinetics of MB adsorption on the SSSC was found to follow a pseudo second-order rate equation.

• The mean free energies (E) revealed that, adsorption of dyes on SSSC seems to be a complex phenomenon, where diffusion and chemical bonding occur at different temperature ranges.

• The values of thermodynamic parameters indicate that all adsorption processes are exothermic, and this is in agreement with the stability of adsorption capacity with temperature.

• Thermodynamic studies are performed and the values of the parameters suggest that the process of removal of MB by SSSC is a spontaneous one.

References

1. Heuzé V, Tran G, Hassoun P, Lebas F, Lessire M (2012) Sunflower hulls and sunflower screenings. Feedipedia.org. A programme by INRA, CIRAD, AFZ and FAO.

2. Gang S, Weixing S (1998) Sunflower stalks as Adsorbents for the removal of metal ions from wastewater. Ind Eng Chem Res 37: 1324-1328.

3. ZongShan ZHAO, JingFu LIU, Chao TAI, ZHOU QunFang, HU JingTian, et al. (2008) Rapid decolorization of water soluble azo-dyes by nanosized zero-valent iron immobilized on the exchange resin. SCIENCE CHINA Chemistry 51: 186-192.

4. Wong YC, Szeto YS, Cheung WH, McKay G (2008) Effect of temperature, particle size and percentage deacetylation on the adsorption of acid dyes on chitosan. Adsorption 14: 11-20.

5. Fujita K, Taniguchi K, Ohno H (2005) Dynamic analysis of aggregation of methylene blue with polarized optical waveguide spectroscopy. Talanta 65: 1066-1070.

6. Waranusantigul P, Pokethitiyook P, Kruatrachue M, Upatham ES (2003) Kinetics of basic dye (methylene blue) biosorption by giant duckweed (Spirodela polyrrhiza). Environ Pollut 125: 385-392.

7. Pereira MFR, Soares SF, Orfao Jose JM, Figureueiredo JL (2003) Adsorption of dyes on activated carbons: influence of surface chemical groups.Carbon 41: 811-821.

8. Cooper P (1993) Removing colour from dyehouse wastewaters - a critical review of technology available, J Soc Dyers Colour 109: 97-100.

9. Stott R, Jenkins T, Bahgat M, Shalaby I (1999) Capacity of Constructed Wetlands to Remove Parasite Eggs from Wastewaters in Egypt. Water Science and Technology 40: 117-123.

10. Kudo K, Hosada H, Honma S, Komatsu M (1973) Studies on the Production of Active Carbon from Coals by Fluidized Bed Reactors J Fuel Soc Jpn 52: 336-344.

11. Barton SS (1987) The adsorption of methylene blue by active carbon. Carbon 25: 343-350.

12. GonzaAlez-Garcia CM, Denoyel R, GonzaAlez-Martin ML, Gomez- Serrano V (2001) Influence of porosity on the adsorption enthalpies of a non-ionic surfactant onto carbonaceous materials. Thermochimica Acta 375: 177-185.

13. Wang LK, Leonard RP, Wang MH, Goupil DW (1975) Adsorption of dissolved organics from industrial effluents on to activated carbon. Journal of Applied Chemistry and Biotechnology 25: 491-502.

14. Zouboulis AI, Lazaridis NK, Zamboulis D (1994) Powdered Activated Carbon Separation from Water by Foam Flotation. Separ SciTechnol. 29: 385-400.

15. Weinberg H, Narkis N (1987) Physico-chemical treatments for the complete removal of non-ionic surfactants from effluents. Environ Pollut 45: 245-260.

16. Dusart O, Souabi S, Mazet M (1990) Elimination of surfactants in water treatment by adsorption onto activated carbon. Environ. Technol. 11: 721-730.

17. http://www.ams.usda.gov/AMSv1.0/getfile?dDocName=STELPRDC5100194

18. Gaikwad RW, Kinldy SA (2009) Studies on Auramine Dye Adsorption on Psidium Guava leaves. Korean J Chem. Eng. 26: 102-107.

19. Demirbasa, E, Kobyab M, Senturkb E, Ozkana T (2004) Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. Water SA 30: 533-540.

20. El-Halwany MM (2007) Development of Activated Carbon from Egyptian Rice Hull: Evaluation of Adsorption Properties (Part I). International Chemical Science Conference Sharm El-Sheikh 16-19 April.

21. El-Halwany MM, Farrag TE (2010) Study of Kinetic Models and Isotherms for Methelyne Blue Adsorption on Corn Straws Pulp as Biosorbent Waste Agriculture Material. International Engineering Conference Mansoura-Sharm El-Sheikh 18-23 Mars.

22. Rashed IG, Al-Sarawy AA, El-Halwany MM, Rabee R (2010) Evaluation of Adsorption Properties for Corn Straws Pulp as Biosorbent Waste Agriculture Material. International Engineering Conference Mansoura-Sharm El-Sheikh 18-23 Mars.

23. El-Halwany MM (2010) Study of Adsorption Isotherms and kinetic Models for Methylene Blue Adsorption on Activated Carbon Developed from Egyptian Rice Hull (Part II). Desalination 250: 208-213.

24. El-Halwany MM (2009) Thermodynamic Functions and Kinetic Models for Methelyne Blue Adsorption on Corn Straw Pulp. Mansoura Engineering Journal 4: 15-24.

25. Farrag TE, El-Halwany MM (2009) Kinetic Models for Methylene Blue Adsorption Using Activated Human Hair Waste as a Biosorbent. Alexanderia Engineering Journal 3: 355-364.

26. DemirbasŸ E, Kobya M, Oncel S, Sencan S (2002) Removal of Ni(II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies. Bioresour Technol 84: 291-293.

27. Dinesh M, Kunwar PS, Gurdeep S, Kundman K (2002) Removal of dyes from wastewater using flyash, a low-cost adsorbent. Ind Eng Chem Res 41: 3688-3695.

28. Muhamad N, Parr J, Smith DM, Wheathey DA (1998) Adsorption of heavy metals in show sand filters in: Proceedings of the WEDC Conference Sanitation and Water for All Islamabad Pakistan 346-349.

29. Jalali R, Ghafourian H, Asef Y, Davarpanah SJ, Sepehr S (2002) Removal and recovery of lead using nonliving biomass of marine algae. J Hazard Mater 92: 253-262.

30. http://www.methuen.co.uk/

31. http://pubs.acs.org/doi/abs/10.1021/la00034a009

32. Romero-Gonzalez J, Peralta-Videa JR, Rodriguez E, Ramirez SL, Gardea-Torresdey JL (2005) Determination of thermodynamic parameters of Cr(VI) adsorption from aqueous solution onto Agave lechuguilla biomass. J Chem Thermo 37: 343-347.

33. El-Dien IM, Al-Sarawy AA, El-Halwany MM, Badawy AA (2013) Evaluation of grinding Salix leaves (gsl) as new sorbent material. J Desalination and water treatment 51: 2564-2574.

34. http://www.ejbiotechnology.info/index.php/ejbiotechnology/rt/printerFriendly/v7n2-Sl1/526#54

35. http://iopscience.iop.org/0004-637X/541/1/120/fulltext/51893.text.html

36. https://www.agronomy.org/publications/sssaj/abstracts/44/2/SS0440020265?access=0&view=pdf

37. http://books.google.com.sa/books?id=8MXX01Qw_G0C&pg=PA208&lpg=PA208&dq=Weber,+W.+J.,+Jr.+%26+Morris,+J.+C.+(1963)&source=bl&ots=oUHN8K29FA&sig=hR8dcaJRIXRLVpqSn_rF8bCt0no&hl=ar&sa=X&ei=Cd2oUa6OCIea1AXozoDgDw&ved=0CHcQ6AEwCQ#v=onepage&q=Weber%2C%20W.%20J.%2