Removal of Sunset Yellow by Methanol Modified Walnut Shell

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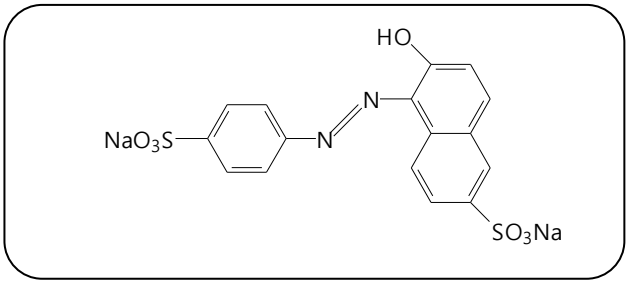
ABSTRACT: *The present research was aimed to analyze the possibility of a novel low-cost biosorbent, Methanol Modified Walnut Shell (MMWS), to improve its biosorption properties with respect to the removal of Sunset Yellow (SY) from aqueous solution, The influences of process parameters, such as pH, temperature, and initial concentration of SY on its adsorption capacity were investigated in a batch system. The equilibrium data were evaluated using the Langmuir and the Freundlich models and the latter could provide a better fit. The Langmuir maximum adsorption capacity of SY onto MMWS was 18.35 mg/g at 298 K, which showed a significant improvement as compared to the raw walnut shell. The obtained thermodynamic parameters demonstrated a spontaneous and endothermic nature of the adsorption process of SY onto walnut shell biomass. The adsorption kinetics fitted well with the pseudo-second-order model. It was concluded that intra-particle diffusion was one of the rate-controlling steps in this process. MMWS was proved to be a promising adsorbent to treat dye wastewater.*

KEYWORDS: *Walnut shell; Adsorption; Sunset yellow; Modification; Mechanism.*

INTRODUCTION

Million tons of synthetic dyes and pigments are produced every year and widely utilized in a variety of industries, including printing, textiles, leather, paper, plastics, food, etc. Many dyes are usually difficult to be biodegraded because of their complicated structure and properties. Besides, some of the dyes, especially azo dyes, are either toxic, teratogenic, or even carcinogenic[1]. The direct discharge of such dye wastewater will cause serious safety hazards and environmental problems. Among the most useful dyes, SY, a pyrazolone dye is widely used in foods, cosmetics, and pharmaceuticals. Although it is not regarded as acutely toxic, SY may cause urticaria, asthma, and many other health problems or environmental problems[2]. And therefore, the maximum dosage of SY was strictly prescribed in National Standard GB 2760-1996 Sanitary Standards of Using Food Additives. The structure of SY is given below.



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At present, many technologies have been developed to remove dyes from wastewater, including advanced oxidation, aerobic and anaerobic digestion, adsorption, membrane filtration, and flocculation [3]. Among these methods, adsorption shows good performance for the treatment of dye wastewater. Activated carbon is the most widely used adsorbent to remove dyes because it shows good adsorption properties and chemical stability. Since the operation cost is still very expensive, people are trying to find more economical and efficient adsorbents to accomplish it. And now an alternative has been successfully explored from different agricultural and forestry wastes such as peanut husk [4-5], internal almond shell [6], sawdust [7], banana peel [8], coconut coir dust [9], etc.

Walnut shell, an abundant agricultural residue, has been successfully used to remove contaminants from wastewater due to its good adsorption property, excellent mechanical strength, and good chemical stability. Efficient removal of metal ion of Cr(VI) [10] and dye of methylene blue from aqueous solution[11-12] have been achieved by introducing a walnut shell as a low-cost adsorbent directly. However, Because of two major limitations, the raw walnut shell may not be suitable for direct use as a good natural adsorbent. Firstly, the soluble component in the walnut shell will dissolve in water, and make the water appear light yellow; secondly, long-term contact with water will cause the walnut shell to be decomposed in the bulk solution and give off an unpleasant smell. Furthermore, an appropriate chemical modification of biosorbents has been proved to be effective to improve the impurity removal efficiency [13-17]. And researchers have found that the adsorption performance of the walnut shell towards different dyes could be efficiently improved by chemically modification with epichlorohydrin and diethylenetriamine [18], and by being impregnated with nano-magnetite Fe_3O_4[19].

Conducted preliminary studies revealed that the raw walnut shell rarely or never adsorbed SY. And therefore, modification chemically with methanol was introduced to prepare a kind of new adsorbent, and its abilities to remove SY from aqueous solutions were compared depending on the initial SY concentration, contact time, and temperature. The mechanisms were deduced with equilibrium, kinetics, and thermodynamics. The work aims at developing an economic and promising biosorbent from the walnut shell for the removal of dyes in wastewater.

EXPERIMENTAL SECTION

Preparation of Methanol Modified Walnut Shell (MMWS)

The walnut shell used in this work was purchased from a local farmers' market. The walnut shell was first immersed in water for 24 h, and then rinsed thoroughly with deionized water to remove impurities dissoluble in water. After that, it was placed in an air-circulating oven and dried for 24 h at 60 ℃. To obtain the adsorbent with uniform particle size, the walnut shell was grounded and sieved below 60 mesh size.

50 mL of methanol (AR) and 0.6 mL of HCl (AR) were mixed with 1.0 g of the raw walnut shell. Then the mixture was placed in a water bath to react for 3.5 h at the temperature of (75 ± 1) ℃. The obtained methanol-modified walnut shell (MMWS) was filtered and rinsed thoroughly with deionized water until the effluent was neutral. And then it was finally dried in an oven for 24 h at 60 ℃ and kept in a dryer.

The modification process can be expressed as follow [20]. This method was based on an alfalfa biomass modification to remove lead [21].

Chemicals

1.0 gram of SY (Analytical Reagents Grade) was dissolved into 1 L of deionized water to prepare the stock solution, which was then diluted to the desired concentration ranging from 50 to 300 $mg \cdot L^{-1}$to prepare sample solutions. The initial pH of sample solutions was adjusted by pH meter (FE20, Mettler Toledo) to a preset value (1.00 - 12.00) ± 0.10 through 1.0 mol/L of the sodium hydroxide or hydrochloric acid solution before the adsorbent was added.

Adsorption studies

0.2 g of MMWS was added to 100 mL of SY solutions at the desired concentration in conical flasks, which were agitated on a shaker(SHA-C Digital Display Thermostatic Oscillator, Jiangsu Dazhong Instrument Co. Ltd, China) at constant 100 rpm and constant temperature. Test samples were taken from the mixture to determine the residual concentration of SY solution at 482 nm spectrophotometrically (UV1102 Spectrophotometer, TECHCOMP, China). All experiments were repeated three times to ensure the accuracy of the data and average values were used for subsequent analysis.

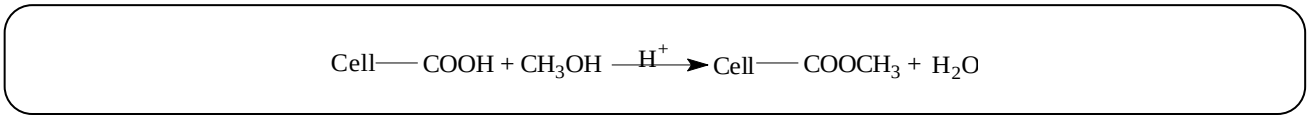

Fig. 1: The preparation scheme of MMWS.

The adsorption capacity q (mg·g^{-1}) was calculated in the following.

$$q = \frac{v(c_0 - c_t)}{m} \quad (1)$$

Where c_0 (mg/L) is the initial concentration, c_t (mg/L) is the concentration at time t, v (L) the volume of SY solution and m is the weight of the MMWS used(g).

For isotherms studies, 0.2 g of MMWS was added to a series of flasks containing 100 mL of SY solution at the desired concentration. The adsorption was conducted at a temperature of 298, 313, and 328K for 4.5 h, respectively.

The Langmuir, the Freundlich, and the Temkin isotherms were used to describe the present system in this work. Non-linear forms of adsorption isotherms were presented in the following.

$$q_e = \frac{q_{max} K_L c_e}{1 + K_L c_e} \quad (2)$$

$$q_e = k_F c_e^{1/n} \quad (3)$$

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln c_e \quad (4)$$

Where c_e (mg/L)is the equilibrium SY concentration, q_e (mg/g) *is* the capacity at equilibrium, q_{max} (mg/·g) is the maximum Langmuir adsorption capacity, K_L (L/mg) the Langmuir equilibrium constant, k_F (L/mg) the Freundlich equilibrium constant, n (dimensionless) a constant related to the heterogeneity of the adsorbent, b (J/mo) the Temkin constant related to the heat of adsorption, K_T (L/g) the Temkin isotherm constant, R (8.314 J/mol.K) the ideal gas constant and T (K) is the absolute temperature of the solution.

For kinetic studies, solutions with the same initial SY concentration were added into a series of flasks, an individual flask was taken out to measure the residual concentration at each predetermined time interval.

The pseudo-first order[22], pseudo-second-order [23], the intraparticle diffusion[24], and the Elovich models were proposed to elucidate the rate-controlling step of this process.

$$q_t = q_e \left(1 - e^{-k_1 t}\right) \quad (5)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (6)$$

$$q_t = k_p t^{0.5} + C \quad (7)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (8)$$

Where q_t (mg/g) is the adsorption capacity at time t (min^{-1}), q_e (mg/g) is the calculated capacity. k_1 (min^{-1}) is the rate constant for the first order, k_2 (g/mg·min) the rate constant for the second-order, k_p (mg/min$^{1/2}$·g) the rate constant for the intraparticle diffusion models, C (mg/g) is a parameter related to the boundary layer, α (mg/g.min) is the initial adsorption rate, and β (g/mg) is the Elovich constant.

The kinetic and isotherm data were nonlinearly fitted using the software of Microcal OriginPro 8.5.1.

Determination of thermodynamic parameters

Thermodynamic parameters, including free energy change (ΔG), enthalpy (ΔH), and entropy change (ΔS) are vital to determine spontaneity and heat changes of an adsorption process. The isosteric enthalpies ΔH were given by the Clausius-Clapeyron equation[25]. The Gibbs free energy values ΔG (kJ/mol) for a system where equilibrium data could be fitted with the Freundlich isotherm can be calculated using Eq. 10 [26]. The entropy change ΔS (J/mol.K) was obtained by the Gibbs-Helmholtz equation [26].

$$\ln c_e = \frac{\Delta H}{RT} + \text{constant} \quad (9)$$

$$\Delta G = -nRT \quad (10)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (11)$$

Where T (K) is the absolute temperature, R (8.314J/mol.K) the universal constant and n is the Freundlich constant.

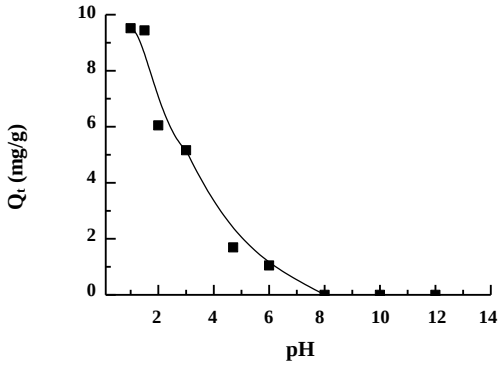

Fig. 2: Effect of pH on the adsorption of SY (T = 298 K, c_0 = 104.4 mg·L^{-1}, contact time = 4.5 h, rpm = 100)

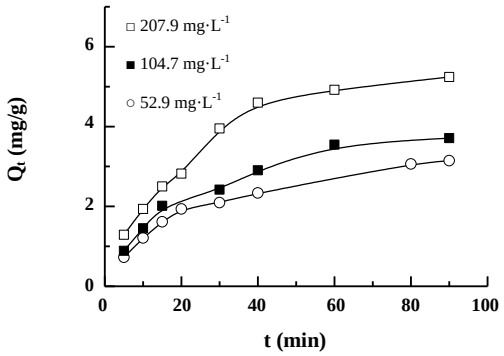

Fig. 3: Effect of contact time on the adsorption of SY (T = 298K, pH = 1.9, rpm = 100).

RESULTS AND DISCUSSION

Effect of Initial pH of the solution

As shown in Fig. 2, pH showed a significant effect on the adsorption of SY onto MMWS. The adsorption of SY decreased sharply with increasing pH from 1.0 up to 8.0, with an optimum value at pH 1.0-2.0. Blank experiments were also conducted under different pH values at the same time, and the solution was found to be clear without any turbidity and opalescent effects, and the concentration of the solution kept also unchanged, which could indicate that there was no chance of the precipitation or conversion of the form of the dye in acid.

In the aqueous solution, SY is dissolved and the sulfonate groups of the anionic dye(D-SO_3Na) are dissociated and converted to anionic ions(D-SO_3^-)[27-28]. At low pH values, the enhanced protonation of -NH_2 on the surface of MMWS made it positively charged, which would be favorable for the association between the positively charged surface of MMWS and the negative SY molecules. With increasing pH values, protonation reduced and the surface of MMWS became more negatively charged, the dominant electrostatic repulsive force would inhibit the diffusion of SY onto MMWS. Furthermore, the anionic dye must be in competition with the OH^- in the solution at high pH values. Similar behaviors were also reported in the adsorption of SY onto other adsorbents [28-30] and methyl orange onto aminated pumpkin seed powder[31].

Effect of Contact Time

The removal of SY by MMWS was performed with the initial concentrations of SY varied from 52.9 to 207.9 mg/L at temperature 298 K and results are shown in Fig.3.

As seen, the adsorption of SY proceeded very fast in the first 40 minutes and then tapered off to approach equilibrium finally at about 100 minutes. The initial high rate was due to numerous vacant sites available on the surface of MMWS at early stages. Then with increasing time, these vacant sites were gradually occupied, the repulsive forces between SY molecules and solution increased, the adsorption process became slower [32].

The equilibrium uptake capacity of the MMWS increased from 3.15 to 5.24 mg/g when the initial SY concentration increased up to 207.9 mg/L. The increase in initial SY concentration enhances the interaction force, which will provide an important driving force to overcome all mass transfer resistance[33-34].

Adsorption Isotherms Parameters

The adsorption isotherms of MMWS were depicted in Fig.4, together with the nonlinear fit with the Freundlich isotherm model. As observed from Fig.4, the adsorption capacity increased with increasing temperature from 298 K to 328 K, which indicated that the adsorption of SY onto MMWS was endothermic.

The adsorption parameters were calculated using Eqs. (2–4) were presented in Table 1. The correlation coefficient R^2 values confirmed that the Freundlich isotherm exhibited a much better fit to the equilibrium data under the studied conditions (all near 0.99), which indicated a heterogeneous MMWS surface and the existence

Table 1 Isotherm model parameters for SY on MMWS

T / K	Langmuir			Freundlich			Temkin		
	q_{max} / mg · g^{-1}	10^2K_L / L· mg^{-1}	R^2	n	k_f	R^2	10^2K_T	b/ J·mol^{-1}	R^2
298	18.35	0.76	0.9906	1.716	0.5098	0.9870	5.98	544.81	0.9854
313	16.34	1.32	0.9748	1.938	0.7770	0.9945	7.90	597.50	0.9744
328	15.67	1.61	0.9483	2.061	0.9551	0.9903	9.47	641.77	0.9708

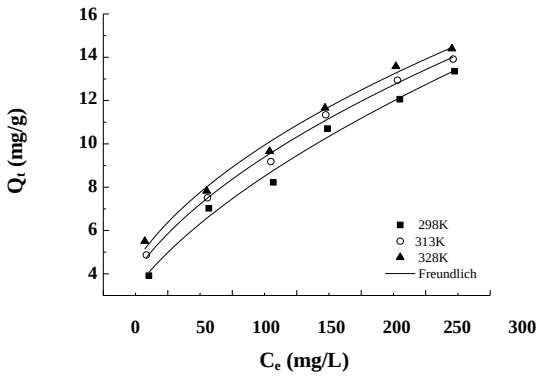

Fig. 4: Adsorption isotherms of SY on MMWS (pH = 1.5, contact time = 4.5 h, rpm = 100).

of interactions between adsorbed molecules[35]. This result was also confirmed by the high correlation coefficient R^2 values of Temkin isotherm(all above 0.96)[36]. For that reason, the nonlinear fit with the Langmuir isotherm was not given in Fig.4. The values of the Freundlich constant, k_f, also increased with increasing temperature, which showed an easier uptake of SY by MMWS at higher temperatures [37]. *n* values greater than 1 were high enough for SY adsorption onto MMWS[38].

The Langmuir maximum adsorption capacity of MMWS for SY listed in Table 1 was 18.35 mg · g^{-1} at 298 K, which was improved significantly when compared with that of the raw walnut shell (almost zero for SY adsorption).

Thermodynamic parameters

Thermodynamic parameters were calculated with Eqs. (9-11) and the results were shown in Table 2. The isosteric enthalpies ΔH were calculated from the slope of the straight line between $\ln c_e$ vs. $1/T$(Fig.5) at different adsorption levels. As can be deduced from Table 2, positive values of all enthalpies < 40 kJ/mol confirmed an endothermic nature of SY adsorption onto MMWS Enthalpies declined with loading suggested that the MMWS had a heterogeneous surface [25].

The spontaneous nature of the adsorption process was further confirmed by the negative values of ΔG. The positive values of ΔS reflected the affinity of MMWS to SY and also indicated the increased randomness at the MMWS/solution and adsorption medium interface. Similar findings were reported in other literature [39-40].

Kinetic parameters of adsorption

The kinetic parameters, k1, k2, and qe, are calculated by non-linear regression analysis of Eqs. 5-8 were compared in Table 3, together with the correlation coefficients R2. It was observed that the pseudo-second-order model gave a better fit than the pseudo-first-order model for SY adsorption onto MMWS, this behavior is supported by the higher correlative coefficient R2 and the better agreement between $qe_{,cal}$, and q_{exp}. Besides, the Elovich equation also agreed well with the experimental data (all R2 values above 0.97). Given that, a chemical interaction between SY and MMWS based on electron exchange or charge sharing may be happening besides physical adsorption in this process. Similar results have been reported for bezathren adsorption onto bentonite, methylene blue onto clay, and malachite green onto sphagnum peat moss [36, 41-43]. As shown in Fig.6 and Table 3, the adsorption kinetics of SY on MMWS could be described by 2 consecutive steps. The qt in the first portion increased rapidly with time due to the fast film mass transfer of SY from the bulk solution to the surface of MMWS. The second portion demonstrated a gradual adsorption stage from the outer surface to the inside of MMWS, where the intraparticle diffusion is rate-limited [44,45]. As expected, the rate constants kp decreased from external to intraparticle diffusion. Similar discoveries were observed for other systems [46-49].

Table 2: Thermodynamic properties of the systems tested.

q_e [mg/g]	ΔH [kJ/mol]	ΔG [kJ/mol]			ΔS [J/mol·K]		
		298K	313K	328K	298K	313K	328K
5	13.75	-4.25	-5.04	-5.62	65.00	61.89	59.06
10	7.25				61.89	36.74	35.06
15	3.44				59.06	27.12	25.88

Table 3: Statistical results of the application of the kinetic models.

Model			Initial SY concentration / mg/L		
			52.9	104.7	207.9
First order kinetic	k_1 (10^{-2})	Rate constant, min^{-1}	4.46	4.50	4.31
	$q_{e,cal}$	Equilibrium capacity, mg/g	3.09	3.68	5.37
	R^2	Correlation coefficient	0.9702	0.9595	0.9857
Second order kinetic	k_2 (10^{-2})	Rate constant, g/mg·min	1.13	0.97	0.64
	$q_{e,cal}$	Equilibrium capacity, mg/g	3.90	4.64	6.72
	R^2	Correlation coefficient	0.995	0.9905	0.9891
Intraparticle diffusion	k_{p1} (10^{-1})	Rate constant, $mg/min^{1/2}$·g	0.54	0.69	0.70
	R_1^2	Correlation coefficient	0.9997	0.9943	0.9963
	k_{p2}(10^{-1})	Rate constant, $mg/min^{1/2}$·g	0.27	0.32	0.30
	R_2^2	Correlation coefficient	0.9973	0.8962	0.8942
Elovich	α	Rate constant ,mg/g·min	0.38	0.46	0.61
	β	the Elovich constant,g/mg	1.19	0.99	0.66
	R^2	Correlation coefficient	0.9933	0.9835	0.9786
$q_{e,exp}$	Experimental data of the Equilibrium capacity, mg/g		3.93	4.63	6.55

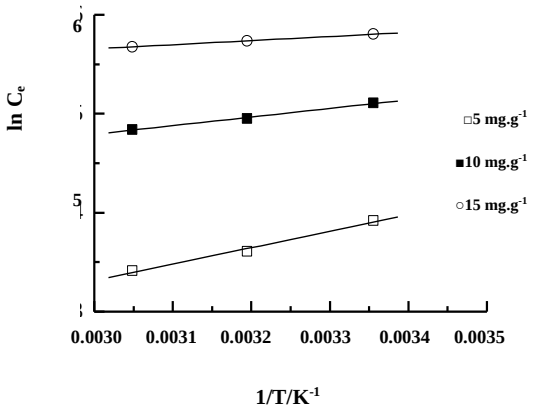

Fig. 5: Isosteric enthalpies of adsorption of SY on MMWS.

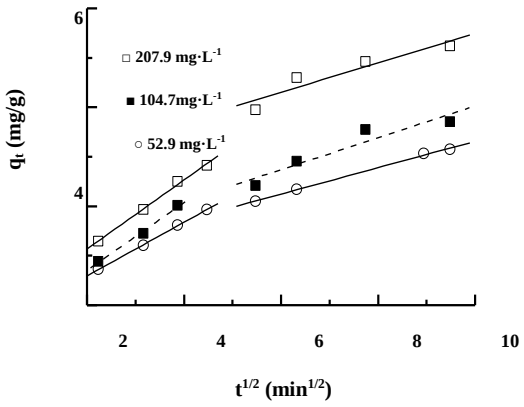

Fig. 6: Intra-particle diffusion model plots at different initial concentrations.

Table 4: Comparison of Adsorption Capacities of Various Adsorbents for SY.

absorbent	Langmuir q_{max} (mg/g)	T (℃)	Adsorbent dosage (g / 100 mL solution)	References
Activated carbon from oak tree wood	5.84–30.12	-	0.1-0.5	[50]
CAT modified Ramulus mori	18.2	25	-	[51]
Unmodified peanut husk	28.9	20	0.33	[4]
Unmodified peanut husk	13.9	20	0.5	[52]
Straw biochar	25.1	-	-	[53]
Macroporous resin D301T	31.5	55	0.25	[54]
Raw walnut shell	0	25	0.2	Present Work
Methanol modified walnut shell	18.35	25	0.2	Present Work

Comparison of SY adsorption on different adsorbents reported in the literature

According to the Langmuir maximum SY adsorption capacities of different low-cost adsorbents listed in Table 4, q_{max} of MMWS for SY was comparable to that of other low-cost adsorbents. MMWS could be used as a promising adsorbent for dye removal from aqueous solutions.

CONCLUSIONS

This study showed that modification of walnut shell with methanol could significantly enhance SY adsorption efficiency. The equilibrium data fitted well with the Freundlich model, and the maximum SY adsorption capacity of MMWS as determined by the Langmuir model was 18.35 mg / g at 298 K. The adsorption kinetics followed he pseudo-second-order model. It can be concluded that the technique presented in this study has an optimistic outlook for practical application in adsorbent modification and SY removal from water.

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