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Removal of Methylene Blue Using Cellulose Nanocrystal Synthesized from Cotton by Ultrasonic Technique

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Authors' contributions

This work was carried out in collaboration between all authors. Author II (AK) designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors YMAO and SMH managed the experimental part and the analyses of the study. All authors managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

This investigation was concern to study the removal of methylene blue pollutants from aqueous solution using cellulose nanocrystal synthesized from cotton. The equilibrium adsorption data were analyzed using adsorption models of Langmuir, Freundlich and Temkin. The thermodynamic parameters were calculated using adsorption process on an cellulose nanocrystal for the methylene blue solution at three different temperatures. It was found that a cellulose at nano level has a very significant adsorption for methylene blue compared to that of bulk cellulose. The results showed that the model isotherms are fitting very well with the experimental data. The specific adsorption percentage of methylene blue was highly affected by addition of nano cellulose and decreasing with temperature compared to that of control sample. It has been found that the adsorption percentage was increased by increasing the methylene blue concentrations, and these values indicated that the methylene blue adsorption onto nano cellulose was spontaneous and exothermic in nature.

All values of Gibbs functions were negative with values of -15 and -17 $kJmol^{-1}$ for 60% acid

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sonicaed for 120 min and 30% acid for the same time of sonification respectively, while values of enthalpy and entropy were about -5 $kJmol^{-1}$ and 54 $JK^{-1}mol^{-1}$ for cellulose nanocrystal respectively. These results indicated that the adsorption process was feasible, spontaneous and exothermic.

Keywords: Cellulose nanocrystal; adsorption; pollution; methylene blue.

1. INTRODUCTION

There are many methods to obtain CNC from natural materials such as mechanical treatments [1-3]. These treatments are including ultrasonification, grinding and high-pressure homogenizer which have been utilized to facilitate the chemical process [4]. Ultrasonic generates a cavitation in the solution and causes micro-bubbles. When micro-bubbles collapse, high energy is released and converted to high pressures and high temperatures. The process causes degradation of chemicals and/or catalytic acceleration of reactions [4-8].

Adsorption is effective in most natural physical, biological, and chemical systems, and is excessively used in industrial applications such as activated charcoal, synthetic resins and water purification [9]. Cellulose is considered to be one of the most economical materials for the elaboration of several types of adsorbent. Cellulose is not only renewable, biodegradable and inexpensive, but it also possesses numerous essential active hydroxyls, which led to various reactions, such as the free radical reaction, esterification, halogenation, oxidation and etherification. Various cellulose derivatives were synthesized by such reactions. Cation-exchange cellulose was modified by quaternary ammonium groups, as adsorption–desorption function groups, to uptake the heavy metal ions from aqueous solutions [10]. As cellulose has amazing hydroxyl groups at the surface, techniques that react with alcohols, e.g. isocyanates, epoxides, acid halides, and acid anhydrides are the most common for direct attachment. These reactions can be used to form a host of alternate surface chemistries such as amine, ammonium, alkyl, hydroxyalkyl, ester (acetate, propionate, etc.), acid, etc [11]. Due to their lack of dispersibility in organic media and polymers, nanocrystalline particle types are very commonly stabilized with surfactants. Sulfuric acid derived CNs provide a charged surface to adsorb surfactants. Such dispersants as stearic acid and cetyltetramethylammonium bromide (CTAB) are widespread [12]. Two main approaches can be used to inoculation polymers onto surfaces, “grafting onto” or “grafting from”, for producing cellulosic nanoparticles with an existing polymer [12].

2. MATERIALS AND METHODS

2.1 Adsorbent

The cellulose nanocrystal (CNC) as adsorbent for adsorption process was synthesized by sonicated raw materials of cotton as described in previous work [13]. Cotton samples were bleached and hydrolyzed with a sulphuric acid at various concentration using vigorous stirring. The suspension was filtered, collected and sonicated by Ultra Sonicator for different periods of time. The subsequent CNC was dried, converted to powder.

2.2 Adsorption Isotherms

2.2.1 Time of equilibrium determination

The equilibrium time was determined by carrying out series of measurements by shaking 0.1 g of prepared CNC with 10 ml of methylene blue (500 ppm) for (10, 20, 30, 40, 50, 60, 90 and 120) min at 200 (rpm/min). This process repeated eight times to preserve the equilibrium time. After completion the shaking process, samples were centrifuged with 4000 (rpm/min) for 20 min was used for the separation. The absorbance of these samples was measured by using UV-visible spectrophotometer at the wave length of 660 nm.

2.2.2 Methylene blue adsorption

Adsorption measurements of methylene blue dye on prepared nano- cellulose was carried out by taking four different concentrations (250, 500, 750, 1000) ppm by adding 10 ml of each concentration to 0.1 g of prepared CNC and placed in conical flasks. The samples were shacked for 60 min at 200 (rpm/min) under three different temperatures (283, 298, 323) K, after that, these samples were filtered using a centrifuge device at 4000 (rpm/min) for 20 min. Equilibrated concentrations of methylene blue was determined by measuring the absorbance using UV-visible spectrophotometer at wavelength of 660 nm. The quantity of adsorbate was calculated by using the following formula [14].

$$Q_e = V_{Sol} (C_o - C_e)/ M$$

Where:

Q_e = Quantity of adsorbate (mg/g)

V_{Sol} = Total volume of adsorbate solution (L)

C_o = Initial concentration of adsorbate solution (mg/L)

C_e = Concentration of adsorbate solution at equilibrium (mg/L)

M = Weight of adsorbate (g)

While the adsorption percentage Q% was calculated by using the following formula.

$$\% \text{ adsorption Efficiency} = (C_o - C_e)/ C_o \times 100$$

Isotherms of Langmuir, Freundlich, Temkin, and Brunauer, Emmet, and Teller (BET) were applied to calculate some adsorption data.

3. RESULTS AND DISCUSSION

3.1 Equilibrium Adsorption

The equilibrium adsorption isotherms are of fundamental importance in the design of adsorption systems [15]. The isotherm of the methylene blue dye adsorption by synthetic cellulose nanocrystal was represented by applying the Langmuir, Freundlich and Temkin adsorption models, and it was found that the adsorption process on the synthetic cellulose nanocrystal fit very well with all isotherm models (Table 1).

The Langmuir equation is

$$Q_e = (Q_o C_e)/(K_L + C_e) \quad (1)$$

Where Q_o is the maximum amount of adsorption corresponding to complete monolayer coverage and K_L is the Langmuir constant. The fitting of adsorption data to Langmuir isotherm equation was investigated by plotting Ce/Qe versus Ce.

Equation 1 is rearranged and gives a straight line as shown in equation 2.

$$C_e/Q_e = (1/K_L Q_o) + (1/Q_o) C_e \quad (2)$$

All Langmuir factors, adsorption data and relations were shown in Table 1, and it is clear that the Langmuir isotherm model fits the analyzed data with its correlation coefficient (R^2).

The Freundlich equation is as following:

$$Q_e = K_f C_e^{1/n} \quad (3)$$

Where, K_f is Freundlich isotherm constant {mg/g], n is adsorption intensity. The constant, K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process. This isotherm is usually used in special cases for heterogeneous surface energy and it is characterized by the heterogeneity factor 1/n. Qe is the equilibrium value of methylene blue dye adsorbed per unit weight of synthetic cellulose nanocrystal, i.e. a liquid-phase sorbate concentration occurred at equilibrium, Kf as the Freundlich constant and 1/n is the heterogeneity factor. On average, a favorable adsorption tends to have Freundlich constant (n) between 1 and 10. Larger value of n (smaller value of 1/n) implies stronger interaction between the adsorbent and the adsorbate. However, Table 1 showed that (n) values were between 1 and 10 emphasizing favorable adsorption of methylene blue dye onto the cellulose nanocrystal. The Freundlich equation was linearized by taking logarithms on each side of the equation and gives a straight line as shown in equation 4.

$$\text{Log } Q_e = \log K_f + 1/n \log C_e \quad (4)$$

All Freundlich factors, adsorption data and relations were shown in Table 1, and it is clear that the Freundlich isotherm model fits the analyzed data with its correlation coefficient (R^2). The Freundlich model assumes that the uptake of any adsorbate occurs on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with increasing the concentration. From these assumptions it can be concluded that synthetic cellulose nanocrystal takes up methylene blue dye on a heterogeneous surface by multilayer adsorption. The linear from of Temkin isotherm is expressed as,

$$q_e = B \ln A + B \ln C_e \quad (5)$$

The adsorption data were analyzed according to eq. (5) and a plot of q_e versus ln C_e enables the determinations of the isotherm constants A and B. The isothermal model of Temkin is based on vapor pressure above a layer of adsorbate that is more than one molecule thick and which resembles a pure bulk liquid [16,17]. Therefore, the adsorption enthalpy changes linearly with pressure [16,18]. Table 1 shows the Temkin factors and relations and it is clear that the Freundlich isotherm model fits the analyzed data with its correlation coefficient (R^2). The rate adsorption of the methylene blue dye increased with increasing of methylene blue dye concentration and the adsorption percentage of methylene blue dye decrease as temperature increase, whereas the adsorption process is an exothermic process (Tables 2, 3 and 4). It can be seen that adsorption capacity increases until an equilibrium concentration is obtained. This confirms a favorable adsorption system. A significant reduction in solution concentration of methylene blue dye was obtained using 0.1 gm of synthetic cellulose nanocrystal for 10 ml of methylene blue dye, at different concentrations and temperatures. There was a decrease in % adsorption efficiency with added adsorbate with slight increase in temperature. Hence it is clearly proved that methylene blue dye adsorption by synthetic cellulose nanocrystal agrees fair enough with all three model isotherms. The correlation coefficient was very high throughout the experimental range of methylene blue dye concentrations studied. However, these results are in a good agreements with other investigations [17,19].

3.2 Thermodynamic Parameters

The thermodynamic parameters ΔG^0, ΔS^0, and ΔH^0 for these adsorption processes are determined by using following equation [19].

$$\Delta G^0 = -RT \ln K \tag{6}$$

Where, K is the thermodynamic equilibrium constant. The effect of temperature on thermodynamic constant is determined by:

$$d \ln K/dt = \Delta H^0/RT^2 \tag{7}$$

$$\text{Log } K = \Delta S^0 / 2.303\, R - \Delta H^0/2.303\, RT \tag{8}$$

Gibbs free energy ΔG^0 is given by:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{9}$$

Table 1. Constant values of methylene blue dye adsorption on nano cellulose under different temperatures

Sample	T (K)	Langmuir const			Freundlich const.			Temkin const.		
		R^2	K_L	A	R^2	N	K_F	R^2	B	KT
30% acid sonicated for 120 min	283	0.967	112.9	0.019	0.987	1.93	6.61	0.96	24.51	0.192
	298	0.928	143.7	0.016	0.992	1.62	5.39	0.94	30.10	0.175
	323	0.967	142.2	0.013	0.992	1.66	4.98	0.91	28.73	0.154
60% acid sonicated for 120 min	283	0.994	129.0	0.014	0.989	1.70	4.89	0.98	28.11	0.141
	298	0.982	155.5	0.014	0.997	1.54	4.83	0.97	31.86	0.160
	323	0.917	139.5	0.011	0.967	1.59	3.97	0.95	29.93	0.116

Table 2. The values of adsorption parameters and amount of adsorption percentage of methylene blue dye on nano cellulose at 283 K

Sample	C_O (MG/L)	C_E (MG/L)	LOG C_E	Q_E (MG/G)	LOG Q_E	C_E/Q_E (G/L)	LN C_E	Q%
30% acid sonicated for 120 min	250	12.70	1.10	23.73	1.38	0.54	2.54	94.92
	500	37.35	1.57	46.27	1.67	0.81	3.62	92.53
	750	91.34	1.96	65.87	1.82	1.39	4.51	87.82
	1000	143.5	2.16	85.65	1.93	1.68	4.97	85.65
60% acid sonicated for 120 min	250	15.16	1.18	23.48	1.37	0.65	2.72	93.94
	500	40.56	1.61	45.94	1.66	0.88	3.70	91.89
	750	80.99	1.91	66.90	1.83	1.21	4.39	89.20
	1000	138.55	2.14	86.15	1.94	1.61	4.93	86.15

Table 3. The values of adsorption parameters and amount of adsorption percentage of methylene blue dye on nano cellulose at 298 K

Sample	C_O (MG/L)	C_E (MG/L)	LOG C_E	Q_E (MG/G)	LOG Q_E	C_E/Q_E (G/L)	LN C_E	Q%
30% acid sonicated for 120 min	250	11.38	1.06	23.86	1.38	0.48	2.43	95.45
	500	31.02	1.49	46.90	1.67	0.66	3.44	93.80
	750	66.19	1.82	68.38	1.84	0.97	4.19	91.18
60% acid sonicated for 120 min	1000	93.30	1.97	90.67	1.96	1.03	4.54	90.67
	250	11.91	1.08	23.81	1.38	0.50	2.48	95.24
	500	31.81	1.50	46.82	1.67	0.68	3.46	93.64
	750	58.47	1.77	69.15	1.84	0.85	4.07	92.20
	1000	94.11	1.97	90.59	1.96	1.04	4.54	90.59

Table 4. The values of adsorption parameters and amount of adsorption percentage of methylene blue dye on nano cellulose at 323 K

Sample	C_O (MG/L)	C_E (MG/L)	LOG C_E	Q_E (MG/G)	LOG Q_E	C_E/Q_E (G/L)	LN C_E	Q%
30% acid Sonicated For 120 min	250	12.78	1.11	23.72	1.38	0.54	2.55	94.89
	500	43.35	1.64	45.67	1.66	0.95	3.77	91.33
	750	71.94	1.86	67.81	1.83	1.06	4.28	90.41
60% Acid Sonicated for 120 min	1000	114.7	2.06	88.53	1.95	1.30	4.74	88.53
	250	17.96	1.25	23.20	1.37	0.77	2.89	92.82
	500	40.56	1.61	45.94	1.66	0.88	3.70	91.90
	750	94.97	1.98	65.50	1.82	1.45	4.55	87.34
	1000	131.1	2.12	86.89	1.94	1.51	4.88	86.89

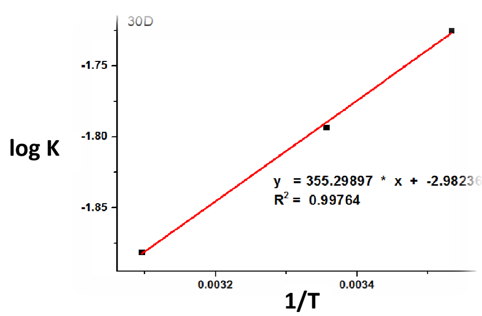

Fig. 1. The plot of log K versus 1/T for MB dye with nano cellulose sonicated for 120 min for 30 % acid

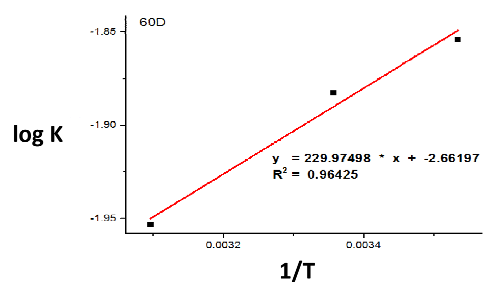

Fig. 2. The plot of log K versus 1/T for MB dye with nano cellulose sonicated for 120 min for 60 % acid

Table 5. Thermodynamic functions of MB dye adsorption of on the NC at different temperatures

Sample	ΔH° kJmol^{-1}	ΔS° Jmol^{-1}K^{-1}	ΔG° kJ.mol^{-1}		
			283 K	298K	323K
30% acid sonicated for 120 min.	-6.80	57.10	-16.17	-17.02	-18.45
60% acid sonicated for 120 min.	-4.40	51.00	-14.43	-15.19	-16.47

Where ΔG^0 is the free energy change (KJ/mol); R is the universal constant (8.314 J/mol K) and T the absolute temperature (K); ΔH^0 change in enthalpy; ΔS^0 is the change in entropy. The ΔH^0 and ΔS^0 values were calculated from slope and intercept of the linear plot, of log K vs. 1/T as shown in Figs. 1 and 2. The corresponding values of thermodynamic parameters are presented in Table 5. The negative values of ΔG^0 indicate that the methylene blue adsorption process is spontaneous and feasible.

The negative value of ΔH^0 shown the adsorption process is exothermic in nature. The positive ΔS^0 values indicated an increase in randomness at the solid/liquid interface during adsorption of methylene blue on carbon. However, the treatment of 30% acid sonicated for 120 min. was favorable compared to that of 60% acid sonicated for the same time, while various temperatures showed no much significant differences.

4. CONCLUSION

The addition of synthetic cellulose nanocrystal as an absorbent to a solution sample of methylene blue reduces, the concentration dramatically. It was found that cellulose at nano level has a very significant adsorption for methylene blue compared to that of bulk cellulose. A high reduction in equilibrium concentration of methylene blue was obtained using 0.1 gm of synthetic cellulose nanocrystal for 10 ml of methylene blue by using different concentrations. The process of adsorption on cellulose nanocrystal fits all isotherm equilibrium adsorption models with a very high correlation coefficient. The adsorption process was feasible, spontaneous and exothermic. Nanoparticles synthesized using cotton processed has to be further investigated for other pollutants.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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