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Thermodynamic Study and Adsorptive Potential of Chicken Egg Shells for the Removal of Acetic Acid from Wastewater

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Abstract

This study is concerned with the thermodynamic properties and the adsorption isotherms of acetic acid adsorption by using the chicken egg shells powder as low cost natural adsorbent, The egg's shell were grinded and sieved after washing with distilled water and Acetone, and dried at 120°C. The concentration of acetic acid was measured before and after adsorption, The amount of acetic acid adsorbed was determined with respect to initial acid concentration, equilibrium time and different acid concentration were obtained manually by titration method. properties of adsorption were determined by applying Freundlich and Langmuir isotherms models to define the thermodynamic properties of this process, adsorption kinetics and thermodynamic parameters ΔH, ΔG and ΔS were calculated. The Results were analysed by applying the Freundlich and Langmuir equations at different temperatures 25°C, 40°C, and 60°C, and determined the characteristic parameters for each adsorption isotherm used (R^2). The Temperature effect has been investigated, the results obtained indicate that the adsorption increase with increasing the temperature. In other words, the adsorption process is of Endothermic type (+ΔH), the results also show that is a spontaneous process (-ΔG) and regular indices (-ΔS), adsorption capacity and intensity were increased with increasing temperature.

Keywords

Adsorption, Egg Shells Powder, Acetic Acid, Freundlich & Langmuir Isotherms

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1. Introduction

Environmental pollution caused by the discharge of untreated poisonous effluents is a major concern of 21st century [1-4]. The industrial effluents cause serious environmental issues because of their adverse effects on the aquatic and terrestrial life as water eutrophication by these substances prevents the penetration of sunlight necessary for photosynthesis [5]. The effluents generated contain toxic substances including dyes, acids, carcinogenic metals, alkalis and aromatic amines. The presence of these substances increases the risk of cancer in human being and is very difficult to remove under aerobic conditions. Among these substances, acids are the main concern as they are soluble in water [6]. Bacteria, fungi, algae, higher plants and some animals secrete organic acids. Important man made sources which participate in the release of organic acids include different products of agriculture, food processing, organic waste, sewage sludge and land fill leachate. As a consequence, organic acids are unfit in ecosphere. Acidic water is dangerous for living organisms on land. The presence of acids also increases the solubility of heavy metals. Acetic acid in waste water is important constituent responsible for unpleasant smell [7]. Various wastewater treatment technologies are based on the process

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of coagulation, flocculation, biodegradation, adsorption, membrane separation, ion exchange, oxidation and selective bio-adsorbents for the elimination of these materials. Because of high cost and disposal problems, many of the conventional methods have not been applied at large scale in different industries. Adsorption has been found to be superior to other techniques in terms of low-cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants [8].

However adsorption is one of the methods, which is gaining more and more attention because of its easy operations and versatility. It is a useful and simple technique and allows kinetic and equilibrium measurements without any highly sophisticated instrument. In adsorption, different adsorbents used include activated carbon [9], zeolite, clays [10], silica beads, and polymeric acids [11] *etc.* However, due to high cost, these materials cannot be justified to cope with pollution and therefore, research has been directed towards methods of treatment using locally available low-cost natural materials such as biopolymers [9]. Consequently, finding simple and easily performable experiments to illustrate the quantitative aspects of adsorption can be very difficult. [12] The importance of adsorption is seen in the need for choosing effective adsorbent for the adsorption or purification needs.

The determination of adsorption capacity is a necessary perquisite for selecting adsorbent. The use of biomaterials as bio-sorbent for the treatment of waste water as a potential alternative to the conventional treatment method has been confirmed in separate studies. [13] various potential adsorbents have been implemented for the removal of specific organics from water. Thus researchers are pursuing hard to develop more suitable, efficient, cheap and easily accessible type of adsorbents. Much work has been carried out using peat [14], sugar cane bagasse [15], biomass [16], eucalyptus bark [17], bottom ash, de-oiled soya [18, 19], hen feathers [20], and egg shells as potential adsorbents.

The objective of the present study to investigate the adsorption potential of powder egg shells as a new low-cost adsorbent for the removal of acetic acid from aqueous solution and wastewater. And to undertake a comparative study of the common adsorption isotherms, Langmuir and Freundlich in the estimation and comparison of quantitative aspect of adsorption. For this present work, egg shells was selected as an adsorbent. Egg shells are waste materials from hatcheries, households and fast food industries and can be

These wastes are directly disposed without any pre-treatment; readily collected in plenty. It is about 11% of the total egg weight and consists of about 95% calcium carbonate and 5% of others materials such as Al_2O_3, SiO_3, S, Cl, Cr_2O_3 and MnO_3.

Egg shells are waste product as about 28% of the total eggs are used commercially in egg products and their disposal contributes to environmental pollution because these cannot be used traditionally [21]. These wastes are directly disposed without any pretreatment; challenges associated with disposal include cost, availability of disposal sites, odor, flies and abrasiveness. However, these egg shells can be used as an excellent adsorbent because of their porous nature; about 700 to 1,700 pores are present on the surface an egg shell [22, 23]. The egg shells are also attractive as adsorbent due to their good mechanical properties and thermal stability [24] and already used as adsorbent for the removal of heavy metals [25], phenolic compounds [8], dyes and pesticides [26].

2. Experimental

2.1. Sample Preparation (Adsorbent)

Chicken egg shells collected from local market (sebha, Libya) were washed with distilled water several times and acetone, followed by drying in a hot air oven at 120°C for (2hrs), and dried in the oven. The dried samples were grinded into powder form and sieved. The powder sample then preserved in different sterilized containers for subsequent use as adsorbent.

2.2. Acetic Acid (Adsorbate)

All solutions were prepared in distilled water. Acetic acid (Panreac, Germany) was used as adsorbate. First stock solution of acid was prepared, and then from this solution, different other working solutions were prepared by dilution method.

2.3. Adsorption Kinetics Study

(1g) of egg shells powder were added in each of different reagent bottles of acetic acid solutions. the bottles were shaken in a thermostat water bath shaker for 20minutes at different temperatures 25°C, 40°C, and 60°C. The slurry obtained after specified time was filtered, pH was noted before and after experiment. The filtrate was titrated against standard NaOH (0.1N) solution to determine change in acid concentration. The amount of acid adsorbed ($C_{\emptyset}$mol·g-1) was calculated by Eq (1):

$$C\emptyset = \frac{(Co - C\sigma)}{S} V \quad (1)$$

where C∅ is the amount of acid adsorbed, Co is the initial concentration and Cσ is equilibrium concentration of the acid, *V* the concentration before adsorption (N_0) was calculated by Eq (2):

$$(C_{eg/L})_0 = N_0 \text{ X } E_w \quad (2)$$

Subsequently, the concentration of acid remaining after adsorption can be calculated by Eq (3):

$$(N\ X\ V)_{(NaOH)} = (N_1\ X\ V_1)_{(CH3COOH)} \quad (3)$$

Where N_1 is the concentration of acid after adsorption.

The amount of acid adsorbed ($Ce_{g/L}$) was calculated by Eq (4): ($N_2 = N_0 - N_1$)

$$(Ce_{g/L}) = N_2\ X\ E_w \quad (4)$$

3. Result and Discussion

3.1. Adsorption Isotherms

The adsorption characteristics of eggshell powder were determined using Freundlich, Langmuir isotherm models [27].

3.1.1. Freundlich Isotherm

The Freundlich parameters were obtained by fitting the experimental data to the linearized equation derived from Eq.(5):

$$logQ_e = logK_f + \frac{1}{n} logC_e \quad (5)$$

Where K_F and n are Freundlich adsorption isotherm constants. being indicative of the extent of the adsorption and the degree of non-linearity between solution concentration and adsorption, respectively; Qe is the amount of acid adsorbed per unit weight of distribution of adsorption sites [28]; Ce the equilibrium concentration (mg/ L). By the logarithmic linearization of Eq. (5)

The following table illustrate the obtained values of adsorption at various temperatures.

Table 1. Calculated Values of Log Ce and Log Qe at Various Temperatures

No	C_e mg /l			Log C_e mg /l			Log Q_e mg/g		
	25°C	40°C	60°C	25°C	40°C	60°C	25°C	40°C	60°C
1	240	470	300	2.62	2.67	2.48	2.3	2.28	2.32
2	600	1260	900	2.77	3.10	2.95	2.62	2.54	2.59
3	1500	2100	1740	3.17	3.32	3.24	2.75	2.7	2.74
4	2400	3300	2940	3.38	3.52	3.47	2.85	2.80	2.82
5	4200	3640	4380	3.62	3.56	3.64	2.9	2.92	2.88

The freundlich isotherm plots for adsorption of acetic acid on egg shells sample are shown in figure 1. According to the linear form of Eq. (5) as given above.

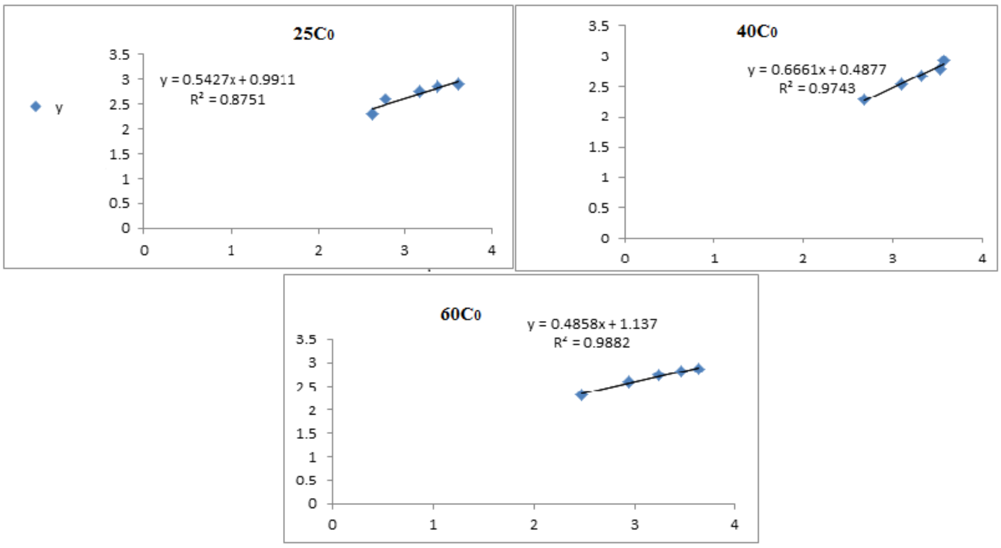

Figure 1. Freundlich isotherm plots for adsorption of acetic acid on egg shell sample.

From the figure 1 which shows Freundlich isotherm plots determine from the high value of R^2 that the model of adsorption also can be characterize by the same equation at temperature higher than 25°C, and the following Table 2 illustrate the constant values of Freundlich equation for adsorption of acetic acid on egg shells.

Table 2. Constant Values of Freundlich Equation for Adsorption of Acetic acid on Egg shells.

T	$\frac{1}{n}$	(n)	Log k	(k)	R^2
25°C	0.542	1.84	0.991	9.8	0.875
40°C	0.666	1.5	0.487	3.1	0.974
60°C	0.485	2.06	1.137	13.7	0.988

The values of *n* and *k* were obtained as given in Table 2. The constant value of n gives information about the surface morphology and the ability of adsorbed solute particles. The efficiency of adsorption increases with increasing *1/n* ratio.

The value of ***k*** (mg/g) indicates the adsorption capacity of powder egg shells. It is clear from the given data in Table 2 that adsorption capacity of egg shell powder increasing temperature.

3.1.2. Langmuir Isotherm

The linear form of this isotherm is given by:

$$\frac{C_e}{Q_e} = \frac{1}{ab} + \frac{C_e}{a} \quad (6)$$

Where *a* (mg/g) is the amount of adsorbed acetic acid in complete monolayer coverage and *b* (mg/l) is the binding energy constants.

Table 3. Calculated Values of Ce, Qe and Ce/Qe at Various Temperatures.

No.	Co g/l	C_e mg /l			Q_e mg/g			C_e/Q_e		
		25°C	40°C	60°C	25°C	40°C	60°C	25°C	40°C	60°C
1	2.4	420	470	300	200	190	210	2.1	2.5	1.4
2	4.8	600	1260	900	420	250	390	2.4	3.6	2.3
3	7.2	1500	2100	1740	570	510	550	2.6	4.1	3.1
4	9.6	2400	3300	2940	720	630	670	3.3	5.2	4.4
5	12	4200	3640	4380	780	755	760	5.4	5.8	5.8

By plotting Ce/Qe against Ce, from the values given in table 3, a straight line was obtained as shown in figure 2.

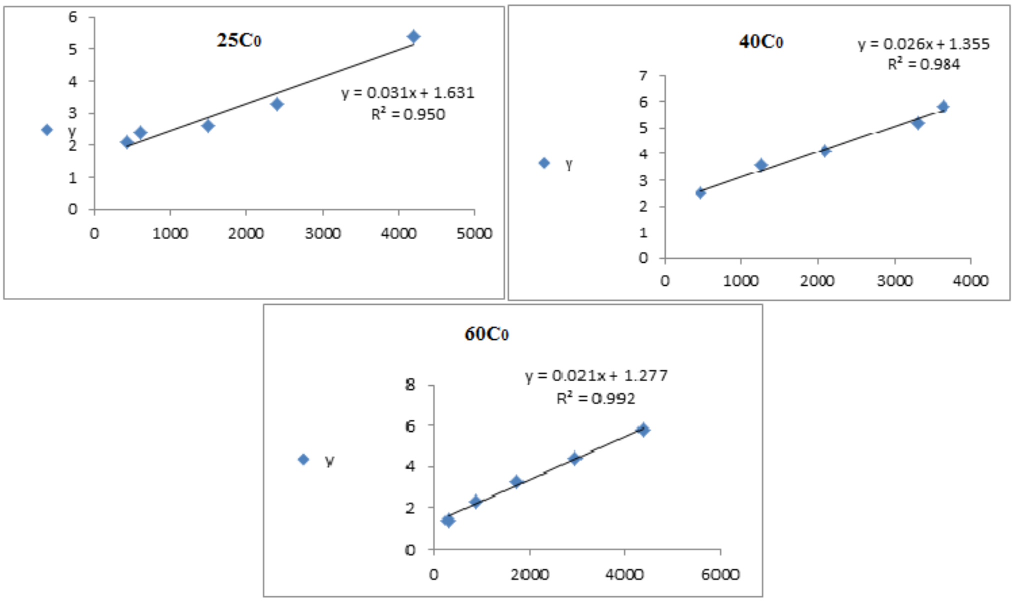

Figure 2. Langmuir Isotherm plots for adsorption of acetic acid on Egg shell sample.

From the plot the values of *a* and *b* were calculated as shown in table 4.

Table 4. Constant Values of Langmuir Equation for Adsorption of Acetic acid on Egg shells.

T	$\frac{1}{a}$	(a) mg/g	$\frac{1}{ab}$	b (mg/l)	R^2
25°C	0.031	32.25	1.631	13.07	0.95
40°C	0.026	38.46	1.355	15.19	0.98
60°C	0.021	47.61	1.227	17.24	0.99

It is apparent from the graph that adsorption capacity of the adsorbent increases with increasing temperature. The regression coefficient R^2 is almost 1 which shows the Langmuir isotherm model is best fit for the adsorption of acids on egg shells adsorbent.

3.2. Adsorption Thermodynamics

The thermodynamic parameters of the adsorption, i.e. the standard enthalpy $\Delta H°$, Gibbs free energy $\Delta G°$ and entropy $\Delta S°$ were calculated using the following equations:

$$\Delta G = - RTln\ K_L \quad (7)$$

$$Ln\ KL = \Delta S/R - \Delta HT \quad (8)$$

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

Where *R* is the ideal gas constant (kJ mol^{-1} K^{-1}), K_L is the

Langmuir constant and *T* is the temperature.

Table 5. Values of Co and Co/Ce at Various Temperatures.

C_o (mg/l)	C_o/C_e		
	25°C	40°C	60°C
2400	5.71	5.11	8
4800	8	3.81	5.3
7200	4.8	3.43	4.14
9600	4	2.9	3.27
12000	2.8	3.3	2.74

From the values in table 5, which illustrate the Co and Co/Ce values at various temperature, were plotting in figure 3.

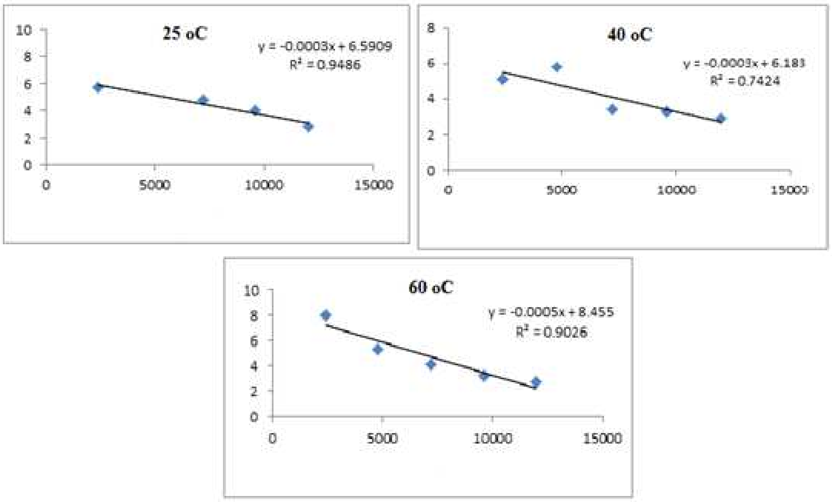

Figure 3. Plots for Co and Co/Ce Values at Various Temperatures.

From the graph the thermodynamic constant which appear in straight linear equation as shown in Table 6 and figure 4.

Table 6. Values of Lin K and 1/T.

parameter	25°C	40°C	60°C
(1/T)	0.00335	0.00319	0.003
(linK)	1.885	1.822	2.135

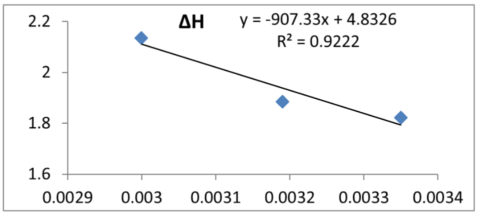

Figure 4. Plot of Enthalpy.

ΔH° and ΔS° values can be obtained from the slope and intercept respectively of Van't Hoff plots of *lin* K_L (from the Langmuir isotherm) versus *1/T*. The results of these thermodynamic calculations are shown in Table 7.

Table 7. Thermodynamic Constants for the Adsorption at Various Temperatures.

(T)	K	ΔH j/mol	ΔG j/mol	ΔS j/mol.K
25°C	6.59		-4670	-40.98
40°C	6.183	7543	-4743	-39.25
60°C	8.455		-5913	-47.39

The negative value for the Gibbs free energy for acetic acid adsorption shows that the adsorption process is spontaneous and that the degree of spontaneity of the reaction increases with increasing temperature. The overall adsorption process seems to be endothermic (ΔH = 7543 J mol^{-1}). This result also supports the suggestion that the adsorption capacity of egg shells for acetic acid increases with increasing temperature.

The values of free energy change ΔG are negative as expected for a spontaneous adsorption process.

4. Conclusion

The application of the constants in the evaluation of quality and the experimental data in the adsorption study was fitted to Freundlich and Langmuir equations to determine the extent and degree of favorability of adsorption. Thermodynamic analysis suggests that removal of acid from aqueous solution by eggshell powder was a spontaneous and endothermic process. Entropy of adsorption has negative value which shows that the acid molecules on the surface of adsorbent take an oriented position. The role of eggshell powder as an adsorbent for removal of acetic acid from aqueous solution has been established.

The present findings suggest that such eggshell is an expensive as a waste material available in many parts of the world, it also can provide a simple, effective and low cost method for waste water purification.

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