Adsorption of Some Alephatic Dicarboxylic Acids on Zinc Oxide: A kinetic and Thermodynamic Study

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Abstract:

The adsorption of Malonic acid, Succinic acid, Adipic acid, and Azelaic acid from their aqueous solutions on zinc oxide surface were investigated. The adsorption efficiency was investigated using various factors such as adsorbent amount, contact time, initial concentration, and temperature. Optimum conditions for acids removal from its aqueous solutions were found to be adsorbent dose (0.2 g), equilibrium contact time (40 minutes), initial acids concentration (0.005 M). Variation of temperature as a function of adsorption efficiency showed that increasing the temperature would result in decreasing the adsorption ability. Kinetic modeling by applying the pseudo-second order model can provide a better fit of the data with a greater correlation coefficient, which indicates that the adsorption process follow the pseudo-second order kinetics. The negative values of Gibbs free energy and the enthalpy change confirm the spontaneous and exothermic nature of the adsorption process. A good ability of zinc oxide to remove aliphatic dicarboxylic acids from its aqueous solutions has been found, and the chain length of the acids has no significant effect on its adsorption.

Key words: Adsorption; Aliphatic Dicarboxylic acids; Zinc oxide.

Introduction:

Water contamination resulting from various artificial processes is a serious problem that requires great attention. Wastewater discharged from agricultural and industrial activities contain both organic and inorganic contaminants (1,2). Usually, organic contaminants undergo oxidation reaction to produce carboxylic acids including dicarboxylic acids as final products (3). Carboxylic acids represent one of the most water-soluble organic material in the nature, which can cause a serious health problems to humans (4).

Adsorption is one of the most recommended methods that has been widely used to treat organic contaminated from water, using different adsorbent materials such as, Activated carbon, clay, chitin, zeolite, metal oxides (5–7). Adsorption is a process that can be defined as the accumulation of a substance (adsorbate) onto the surface of a solid or liquid (adsorbent). It can be classified into two types depending on the attraction forces; Chemical adsorption due to the exchange of electrons, and physical adsorption resulted from physical forces such as Vander Waals forces and polarity (5).

Many researchers reported the use of activated carbon for removal of organic contaminated from water (8–15). Zinc oxide due to its significant physical and chemical properties is considered as a multifunctional material, which can be widely used in different applications (16–18). This study aims to investigate the ability of zinc oxide for the removal of aliphatic dicarboxylic acids from aqueous solution.

Materials and Methods:

All chemicals were used as received. Malonic acid (BDH), Succinic acid (Fluka), Adipic acid (Fluka), Azelaic acid (BDH). ZnO used in the study from May & Baker LTD England (99 % purity, average particle size ~ 5 μm).

In this study, many experiments were conducted in order to investigate the effect of the contact time, adsorbent amount, initial concentration, and temperature. For each experiment, a series of aliphatic dicarboxylic acid solution were prepared by placing a 20 ml of known concentration and ZnO amount in 100 ml conical flask.

Each solution was shaken in a controlled shaking water bath using a constant speed of 120 rpm for about 40 min. under thermostatic condition in order to reach the adsorption equilibrium. The

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solution then filtered, and the supernatant titrated with 0.01 M Sodium hydroxide solution. The amount of aliphatic dicarboxylic acid adsorbed on the surface of ZnO then calculated from the concentration difference.

The adsorption efficiencies are calculated using the equation below:

$$\% \, Adsorption = (C_0 - C_e)/C_0 \times 100 \quad (1)$$

Where, C_0 is the initial concentration (mg/L) of the acid, C_e is the concentration (mg/L) of the acid at equilibrium.

The amounts of acid adsorbed at time t calculated using the following equation (3,8):

$$q_t = (C_0 - C_e)V/m \quad (2)$$

Where, q_t is the quantity of acid adsorbed per gram of adsorbent (mg/g), V is the volume of the acid solution (lit.), and m is the mass of the adsorbent (g).

Moreover, the adsorption kinetic study was performed using two different models, the lagergren's pseudo-first order model (Eq. 3), and pseudo-second order model (Eq. 4):

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)\, t \quad (3)$$

$$t/q_t = (1/k_2\, q_e^2) + (1/q_e)\, t \quad (4)$$

Where q_e is the adsorption capacity (mg/g) at equilibrium, q_t is the adsorption capacity (mg/g) at time t, k_1 is the pseudo-first order rate constant (min^{-1}), k_2 is the pseudo-second order rate constant (g. mg^{-1}. min^{-1}).

Finally, the thermodynamic study for the adsorption of the acids on ZnO was evaluated using the following equations:

$$\Delta G^\circ = -\, RT \ln K \quad (5)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

$$\ln K = (\Delta S^\circ/R) - (\Delta H^\circ/RT) \quad (7)$$

Where, R is the gas constant (8.314 J/mol K), T is the absolute temperature (K), ΔH° is the enthalpy change (J/mol), ΔS° is the entropy change (J/mol K), ΔG° is the free energy change (J/mol), K is the distribution coefficient of adsorption process, and can calculated using the following equation:

$$K = (C_0 - C_e)/C_e \quad (8)$$

Results and discussion:

Four aliphatic dicarboxylic acids with different chain length were investigated. The chemical structure of these acids is given in Fig. 1.
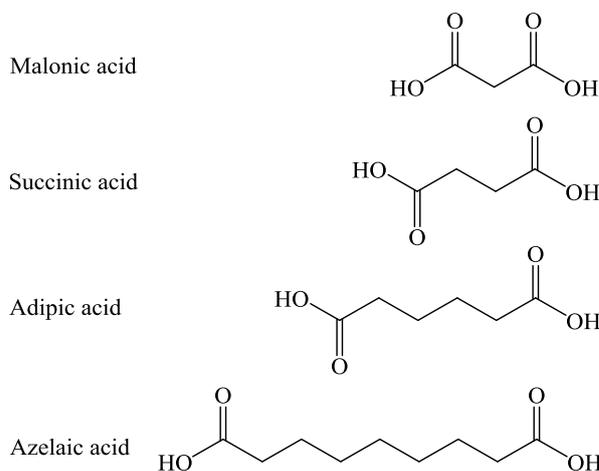
Figure 1. The chemical structure of Malonic acid, Succinic acid, Adipic acid, and Azelaic acid.

The variation of the contact time as a function of adsorption efficiency was investigated. Figure 2 displays the effect of the contact time on the removal of Malonic acid, Succinic acid, Adipic acid, and Azelaic acid by Zinc oxide. There can be seen a fast removal of the aliphatic carboxylic acids by ZnO in the first few minutes. This indicates a high affinity between the acids and the ZnO surface, which corresponds to the existence of a large number of unoccupied adsorption sites on the adsorbent. After that, a gradual increase in the adsorption process is observed as the time going on, and the uptake level becomes slower due to the decrease in the accessible adsorption sites. After 40 minutes, the adsorption process becomes constant, and no further adsorption can take place. This may occur because of the great decrease of the accessible adsorption sites, and the residual sites are hard to occupy due to the resistance between the adsorbate particles on the surface of the adsorbent and the incoming adsorbate particles (3). This indicates that equilibrium point can be reached in about 40 minutes for all considered acids.
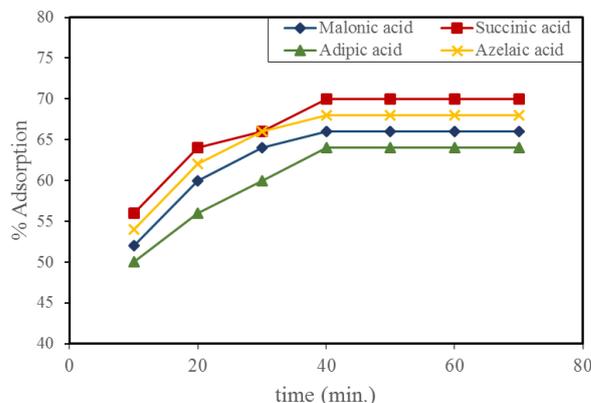
Figure 2. Effect of contact time on the adsorption of Malonic acid, Succinic acid, Adipic acid, and Azelaic acid on ZnO.

The variation of adsorbent dosage was also investigated. Figure 3 represents the effect of ZnO amount on the adsorption of Malonic acid, Succinic acid, Adipic acid, and Azelaic acid. It is more likely that using a small amount of the adsorbent can remove a small amount of the adsorbate, which might be related to the adsorption sites number. Thus, it can clearly be seen that the initial values of the acids removal are very small, and as the amount of ZnO increased, the removal of the acids was also increased to reach its maximum value when using 0.2 gm of the adsorbent. It is possible that increasing the adsorbent amount can provide more accessible adsorption sites that can adsorb more adsorbate particles and thus increase the adsorption percentage(19). After that, the adsorption process becomes constant, because the residual sites are hard to be occupied, thus no further adsorption between the adsorbate particles and adsorbent surface can take place, which is considered to be approaching the equilibrium point.
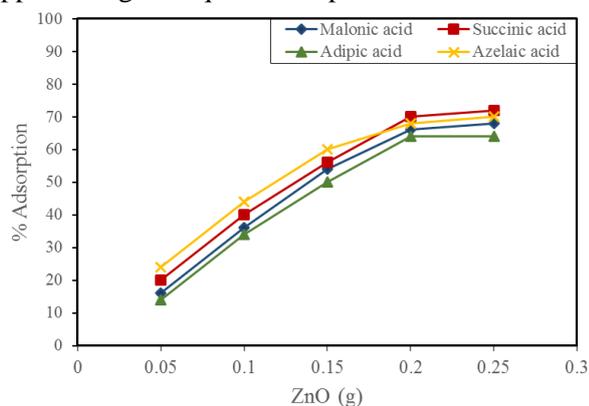
Figure 3. Effect of the ZnO amount on the adsorption of Malonic acid, Succinic acid, Adipic acid, and Azelaic acid.

The effect of the initial concentration on the adsorption efficiency was investigated using different acids concentrations ranging between 0.001 and 0.0125 M, and keeping the other parameters constant. Figure 4 shows the effect of the initial concentration on the adsorption of Malonic acid, Succinic acid, Adipic acid and Azelaic acid on ZnO surface. There can be clearly observed good adsorption efficiency with low acids concentration, and the uptake level continued almost constant with increasing the concentration until reaching 0.005 M. After that, as the acids concentration increases, the removal efficiency decreases. This is probably due to the existence of a large number of free adsorption sites on the adsorbent at the beginning of the adsorption process in comparison with the adsorbate particles number (20). In addition, as the acids concentration increases, the ratio of the adsorbate particles that will occupy the adsorption sites decreases. Thus, the

percentage of the adsorbate removal will decrease and lowering the adsorption efficiency. This indicates that 0.005 M can be considered as the optimal concentration.
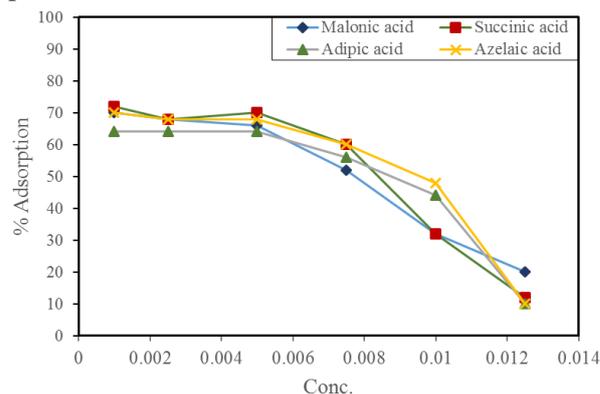
Figure 4. Effect of the concentration on the adsorption of Malonic acid, Succinic acid, Adipic acid, and Azelaic acid on ZnO.

The effect of temperature on the removal of the aliphatic dicarboxylic acids by ZnO was tested using different temperatures in the range of 20-60 °C. Figure 5 displays the effect of the temperature on the adsorption of Malonic acid, Succinic acid, Adipic acid, and Azelaic acid on ZnO. There is clearly good adsorption efficiency at low temperature with initial values of about %70. As the temperature increased, the level of the acid removal decreased for all considered acids. This suggests that adsorption process of the studied acids is an exothermic process, and rising the temperature would result in reducing the adsorption ability (21).
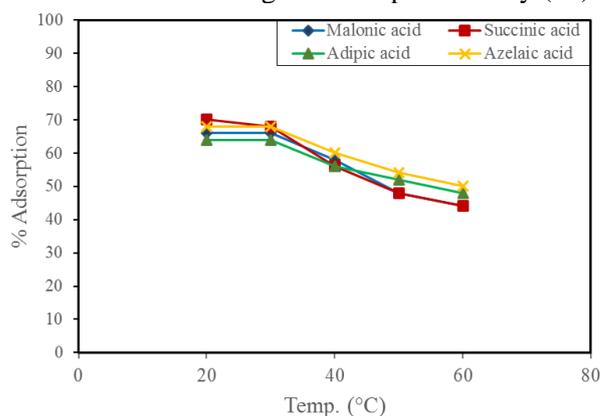
Figure 5. Effect of the temperature on the adsorption of Malonic acid, Succinic acid, Adipic acid, and Azelaic acid on ZnO.

Kinetic studies:
The kinetic studies were carried out to understand the adsorption mechanism during the transfer of acids particles from bulk solution to the adsorbent surface. Two different models were applied in order to investigate the kinetic of acids adsorption on ZnO; the Lagergren's pseudo-first

order rate equation (Eq.3) and pseudo-second order rate equation (Eq.4)

The rate of acids adsorption using pseudo first order model was performed by plotting log (q_e- q_t) versus time (Fig. 6), and the values of k_1 and calculated q_e are obtained from the slopes and intercepts of the straight lines, respectively. Similarly, for the pseudo second order model, the values of k_2 and calculated q_e are determined from the intercepts and the slopes of the straight lines resulted from the plot of t/q_t versus time, respectively Fig. 7.
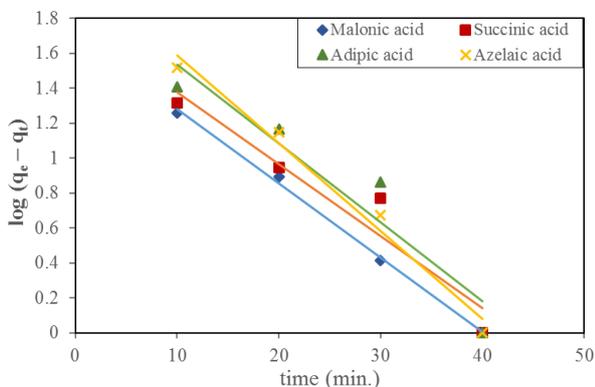
Figure 6. Pseudo-first order kinetic plot for acids adsorption on ZnO surface.
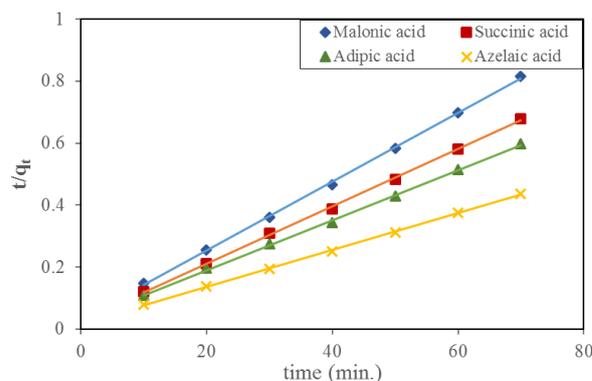
Figure 7. Pseudo-second order kinetic plot for acids adsorption on ZnO surface.

The kinetic parameters for the adsorption of the acids onto ZnO surface obtained from the fitting of kinetic models on the adsorption data are presented in Table 1. The comparison between the experimental and the calculated values of the adsorption capacities (q_e), clarify that the pseudo-second order kinetic model provided a better fit of the data.

Table 1: Kinetic parameters for the adsorption of acids onto ZnO surface.

Pseudo-first order model				
Adsorbate	k_1 (min^{-1})	R^2	q_e cal. (mg/g)	q_e exp. (mg/g)
Malonic acid	0.098108	0.9978	50.82765	85.8
Succinic acid	0.094884	0.9223	61.43276	103.25
Adipic acid	0.104096	0.9038	97.63376	116.8
Azelaic acid	0.115841	0.9817	123.7656	159.9955
Pseudo-second order model				
Adsorbate	k_2 (g. mg^{-1}. min^{-1})	R^2	q_e cal. (mg/g)	q_e exp. (mg/g)
Malonic acid	0.003975	0.9994	90.09009	85.8
Succinic acid	0.00317	0.9994	108.6957	103.25
Adipic acid	0.002255	0.9991	123.4568	116.8
Azelaic acid	0.002236	0.9994	166.6667	159.9955

Moreover, high correlation coefficients were obtained from fitting the tow kinetic models, however, the correlation coefficient of pseudo-second order kinetic model are greater than that for pseudo-first order kinetic model (Table 1). These results confirm that the adsorption process follows the pseudo second order kinetics.

Thermodynamic studies:

Obtaining the thermodynamic parameters can provide a good clarification for the mechanism of the adsorption process. The distribution coefficient of adsorption process (K) was calculated at different temperatures using Eq. 8. The value of Gibbs free energy change $\Delta G°$ was determined using Eq. 5. While, $\Delta H°$ and $\Delta S°$ were obtained according to Van't Hoff equation (Eq. 7), from the slope and intercept of the straight line resulted from the plot of ln K versus 1/T, respectively Fig. 8.
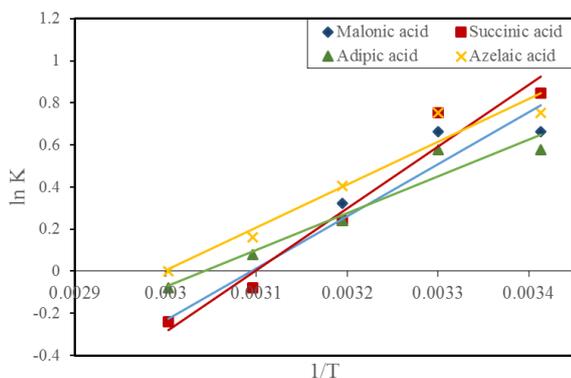
Figure 8. Van't Hoff plot for acids adsorption on ZnO surface.

The thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) for the adsorption of acids onto ZnO surface are listed in Table 2. These parameters were evaluated at various temperatures (20 – 60 °C) with initial concentration of 0.005 M, 0.2 g of adsorbent, and 40 minutes contact time. The negative values of $\Delta H°$ for all acids considered in this study indicate that the adsorption of acids onto ZnO surface is exothermic. This is compatible with the early conclusion, which reveals that the adsorption efficiency decreased with the increase in temperature Fig. 5. In addition, the negative values of $\Delta G°$ indicates that the adsorption process have a spontaneous nature. Furthermore, the negative values of $\Delta S°$ indicate that the randomness increased at the solid/solution interface through the adsorption process.

Table 2: Thermodynamic parameters for the adsorption of acids onto ZnO surface at various temperatures.

Adsorbate	$\Delta H°$ ($J. mol^{-1}$)	$\Delta S°$ ($J. mol^{-1}. K^{-1}$)	$\Delta G°$ ($J. mol^{-1}$)
Malonic acid	-20581.3	63.68108	-1615.79
Succinic acid	-24411.6	75.62248	-2134.46
Adipic acid	-14597.7	44.41921	-1497.26
Azelaic acid	-16968	50.86671	-2024.2

Conclusion:

The adsorption characteristic for the adsorption of aliphatic dicarboxylic acids on zinc oxide has been examined. The optimal values for the removal of aliphatic dicarboxylic acids by zinc oxide are adsorbent dosage 0.2 gm, contact time 40 min., and initial concentration 0.005 M. Kinetic modeling shows that the adsorption process follows the pseudo-second order kinetics with a better correlation coefficient. The thermodynamic parameters emphasizes that the adsorption process

is spontaneous and exothermic in nature. These results indicate that zinc oxide can be utilized successfully for the removal of dicarboxylic acids from aquios solutions, and the chain length of the aliphatic dicarboxylic acid has no important effect on its adsorption.

Conflicts of Interest: None.

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امتزاز بعض الحوامض الاليفاتية ثنائية الكاربوكسيل على أوكسيد الزنك: دراسة حركية وثرموداينميكية

صدام محمد المحمود

قسم الكيمياء، كلية التربية للبنات، جامعة تكريت، تكريت، العراق

الخلاصة:

الهدف من اجراء هذا البحث هو لدراسة ميكانيكية امتزاز حامض المالونيك، حامض السكسنيك، حامض الاديبيك، وحامض الازيلايك من محاليلها المائية على سطح أوكسيد الزنك. حيث تم دراسة كفاءة الامتزاز بالاستعانة بعدة عوامل مختلفة مثل كمية المادة المازة، زمن التماس، التركيز الابتدائي، ودرجة الحرارة. اظهرت النتائج ان الظروف المثلى اللازمة لإزالة الحوامض من محاليلها المائية هي كمية المادة المازة 0.2 غرام، وأفضل زمن للاتزان هو 40 دقيقة، والتركيز الابتدائي للحوامض كان 0.005 مولاري. كما أظهرت الدراسة ان زيادة درجة الحرارة تقلل من كفاءة الامتزاز. ومن خلال تطبيق النماذج الحركية على عملية الامتزاز وجد ان نموذج الرتبة الثانية الكاذبة يعطي علاقة خطية مع معامل ارتباط جيد. كما اشتملت الدراسة على حساب الدوال الثرموداينميكية، حيث أظهرت النتائج ان القيمة السالبة للطاقة الحرة لجبس والتغير في الانثالبي تؤكدان التلقائية والطبيعة الباعثة للحرارة لعملية الامتزاز. لقد وجد ان لاوكسيد الزنك قابلية جيدة على إزالة الحوامض الاليفاتية ثنائية الكاربوكسيل من محاليلها المائية، وان طول السلسلة للحوامض ليس له أي تأثير على امتزازها.

الكلمات المفتاحية: الامتزاز ، الحوامض الاليفاتية ثنائية الكاربوكسيل، أوكسيد الزنك

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