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Insight Into Adsorption Thermodynamics

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1. Introduction

Saving the environment to save the Earth and to make the future of mankind safe is the need of the hour. Over the past several decades, the exponential population and social civilization change, affluent lifestyles and resources use, and continuing progress of the industrial and technologies has been accompanied by a sharp modernization and metropolitan growth. The world is reaching new horizons but the cost which we are paying or we will pay in near future is surely going to be high. Among the consequences of this rapid growth is environmental disorder with a big pollution problem. Rapid industrialization, unplanned urbanization and unskilled utilization of natural water resources have led to the destruction of water quality in many parts of the world. In many developing countries, groundwater provides drinking water for more than one-half of the nation's population, and is the sole source of drinking water for many rural communities and some large cities. However, due to industrial, agricultural and domestic activities, a variety of chemicals can pass through the soil and potentially contaminate natural water resources and reservoirs.

In recent years, the surge of industrial activities has led to tremendous increase in the use of heavy metals, synthetic dyes and other toxic chemicals, and inevitably resulted in an increased flux of these substances in the aquatic environment. Environmental contamination by toxic heavy metals and synthetic dyes is becoming a serious dilemma now days due to their negative ecotoxicological effects and bioaccumulation in wildlife. Contamination primarily result from industrial activities, such as iron and steel production, the non-ferrous metal industry, mining and mineral processing, pigment manufacturing, tanning, dyeing, painting, photographic and electroplating, gas exhaust, energy and fuel production, fertilizer, food, cosmetics, pharmaceuticals, pesticide applications, and generation of municipal wastes. The contamination of water due to toxic heavy metal ions and synthetic dye molecules is accountable for causing several damages to the environment and adverse effects on public health. Heavy metals form compounds that can be toxic, carcinogenic or mutagenic even in low quantities and due to their mobility in natural water ecosystems, they are prioritized as major inorganic contaminants of the environment. Furthermore, heavy metal ions are nonbiodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain. Even, their minor content can bio-accumulate and enter the food chain causing mental retardation, reduction in hemoglobin production and interference with normal cellular metabolism and consequently may damage nervous system. Strong exposure may cause gastric pain, nausea, vomiting, severe diarrhea,

hemorrhage and even cancer in the digestive tract and lungs. On the contrary, synthetic dyes contained in wastewaters may affect photosynthesis by preventing light penetration, thereby compromising aquatic life. Additionally, dye molecules can decompose into carcinogenic aromatic amines under aerobic conditions which can cause serious health problems to humans and animals. Also, dyes can cause allergy, dermatitis, skin irritation and cancer in humans.

With the rising awareness of the occurrences of industrial activities which has intensified numerous deteriorations on several ecosystems and seriously threatens the human health and environment, the enforcement of stringent rules and regulations concerning the emission of contaminants from industrial waste streams by various regulatory agencies has been promulgated. Simultaneously, a developing research by the invention of a wide range of treatment technologies (precipitation, coagulation–flocculation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, biological process, chemical reactions, adsorption, ion exchange, photocatalytic degradation, sonochemical degradation, micellar enhanced ultrafiltration, cation exchange membranes, electrochemical degradation, integrated chemical–biological degradation, integrated iron(III) photoassisted-biological treatment, solar photo-Fenton and biological processes, and Fenton-biological treatment scheme) with varying levels of successes has accelerated a dramatic progress in the scientific community. Of major interest, adsorption, a surface phenomenon by which a multi-component fluid (gas or liquid) mixture is attracted to the surface of a solid adsorbent and forms attachments via physical or chemical bonds, is recognized as the most efficient, promising and widely used fundamental approach in wastewater treatment processes, mainly hinges on its simplicity, economically viable, technically feasible and socially acceptable. Further, this process can remove/minimize different type of pollutants and thus it has a wider applicability in water pollution control. Adsorption separation in environmental engineering is now an aesthetic attention and consideration abroad the nations, owing to its low initial cost, simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions. A large number of natural materials or the wastes/by-products of industries or synthetically prepared materials, which cost less and can be used as such or after some minor treatment have been tested and examined for their ability to remove various types of pollutants from water and wastewater.

At present, adsorption field has been enriched by a vast amount of studies published in different journals. Extensive research has been dedicated to sound understanding of adsorption isotherm and kinetics. However, a study on adsorption can only be meaningful and useful if it includes the structure as well as the dynamics of its different components, separately and interacting with each other. In this regard, it should be realized that an extensive study on adsorption thermodynamics is desirable. Confirming the assertion, this chapter presents a state of art review of adsorption thermodynamics.

In the design of adsorption systems, two types of thermodynamic properties, namely the directly measurable properties like temperature, equilibrium constant, and properties which cannot be measured directly such as activation energy, activation parameters, Gibb's free energy change, enthalpy, entropy, and isosteric heat of adsorption are required. These parameters are critical design variables in estimating the performance and predicting the mechanism of an adsorption separation process and are also one of the basic requirements for the characterization and optimization of an adsorption process. Thus, this chapter attempts to offer a better understanding of adsorption thermodynamics with special focus on its fundamental characteristics and mathematical derivations.

2.1 Activation energy

Activation energy is an important parameter in a thermodynamic study as it determines the temperature dependence of the reaction rate. In chemistry, activation energy is defined as the energy that must be overcome in order for a chemical reaction to occur. In adsorption separation, it is defined as the energy that must be overcome by the adsorbate ion/molecule to react/interact with the functional groups on the surface of the adsorbent. It is the minimum energy needed for a specific adsorbate-adsorbent interaction to take place, even though the process may already be thermodynamically possible. The activation energy of a reaction is usually denoted by E_a, and given in units of kJ mol^{-1}. The activation energy (E_a) for the adsorption of an adsorbate ion/molecule onto an adsorbent surface in an adsorption process can be determined from experimental measurements of the adsorption rate constant at different temperatures according to the Arrhenius equation as follows:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{1}$$

where k is the adsorption rate constant, A is a constant called the frequency factor, E_a is the activation energy (kJ.mol^{-1}), R is the gas constant (8.314 J.$mol^{-1}K^{-1}$) and T is the temperature (K). By plotting ln k versus 1/T (Figure 1) and from the slope and the intercept, values of E_a and A can be obtained. The apparent activation energy of adsorption of heavy metal ions and synthetic dye molecules onto various low cost adsorbents is tabulated in Table 1.

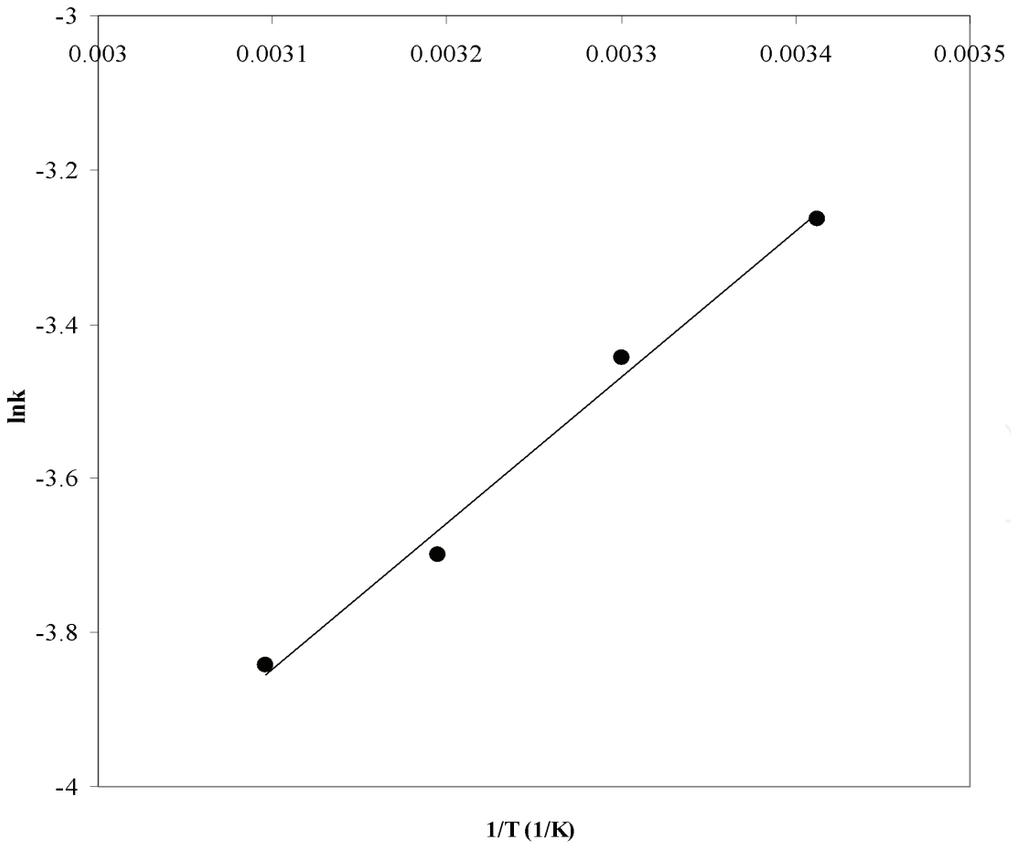


Fig. 1. A typical plot of ln k vs. 1/T (Arrhenius plot)

The magnitude of activation energy may give an idea about the type of adsorption. Two main types of adsorption may occur, physical and chemical. In physisorption, the equilibrium is usually rapidly attained and easily reversible, because the energy requirements are small. The activation energy for physisorption is usually no more than 4.2 kJ mol^{-1} since the forces involved in physisorption are weak. Chemisorption is specific and involves forces much stronger than in physisorption on. Therefore, the activation energy for chemisorption is of the same magnitude as the heat of chemical reactions. Two kinds of chemisorptions are encountered, activated and, less frequently, nonactivated. Activated chemisorption means that the rate varies with temperature according to finite activation energy (between 8.4 and 83.7 kJ/mol) in the Arrhenius equation (high E_a). However, in some systems the chemisorption occurs very rapidly, suggesting the activation energy is near zero. This is termed as a nonactivated chemisorption.

Adsorbent	**Adsorbate**	**E_a (kJ mol^{-1})**	**Reference**
Peanut hull	Cu(II)	17.02	Zhu et al., 2009
Laterite nickel ores	Pb(II)	7.6	Mohapatra et al., 2009
Cation exchanger derived from tamarind fruit shell	Cu(II)	10.84	Anirudhan & Radhakrishnan, 2008
Walnut hull	Cr(VI)	102.78	Wang et al., 2009
Wineyard pruning waste	Cr(III)	-15.65	Karaoglu et al., 2010
Sepioloite	Maxilon Blue 5G	19.25	Alkan et al., 2008
Chemically modified rice husk	Malachite Green	68.12	Chowdhury et al., 2010
Sea shell powder	Malachite Green	15.71	Chowdhury & Saha, 2010
Modified wheat straw	Methylene Blue	24.24	Han et al., 2010
Pinus sylvestris L.	Reactive Red 195	8.904	Aksakal & Ucun, 2010

Table 1. Activation energy for adsorption of heavy metal ions and dye molecules onto various low cost adsorbents

It is to be noted that in some cases rates of adsorption process decrease with increasing temperature. In order to follow an approximately exponential relationship so the rate constant can still be fit to the Arrhenius expression, results in a negative value of E_a. Sorption processes exhibiting negative activation energies are exothermic in nature and proceeds at lower temperatures. With the increase of temperature, the solubility of adsorbate species increases. Consequently, the interaction forces between the adsorbate and solvent are stronger than those between adsorbate and adsorbent. As a result, the adsorbate is more difficult to adsorb

2.2 Activation parameters

In order to get an insight whether the adsorption process follows an activated complex, it is absolutely necessary to consider the thermodynamic activation parameters of the process

such as activation enthalpy (ΔH^*), activation entropy (ΔS^*) and free energy of activation (ΔG^*). The standard enthalpy of activation (ΔH^*), entropy of activation (ΔS^*), and free energy of activation (ΔG^*) in the adsorption process were calculated by the Eyring equation:

$$\frac{\ln k}{T} = \ln \frac{k_B}{\mathrm{h}} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \tag{2}$$

where k is the adsorption rate constant, k_B is the Boltzman constant (1.3807×10^{-23} J K^{-1}), h is the Plank constant (6.6261×10^{-34} Js), R is the ideal gas constant (8.314 $J.mol^{-1}K^{-1}$), and T is temperature (K). The values of ΔH^* and ΔS^* can be determined from the slope and intercept of a plot of ln k/T versus 1/T (Figure 2). These values can be used to compute ΔG^* from the relation:

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{3}$$

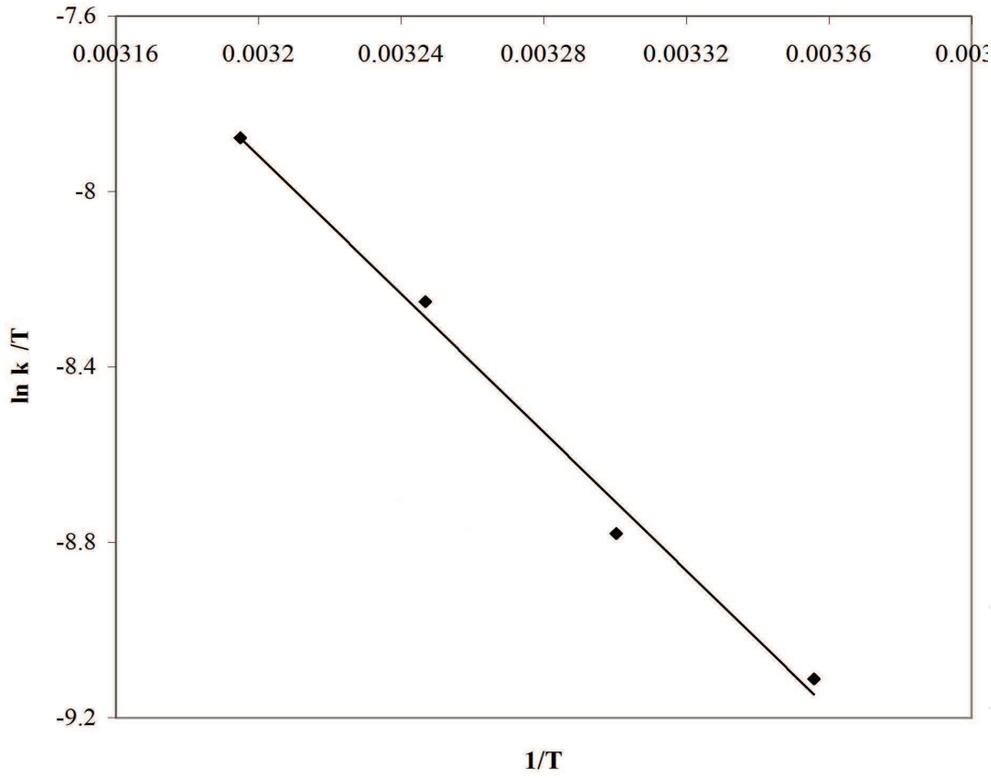


Fig. 2. A typical plot of ln k/T vs. 1/T (Eyring equation plot)

In general, the ΔG^* values are positive at all temperatures suggesting that adsorption reactions require some energy from an external source to convert reactants into products. A negative value of ΔH^* suggests that the adsorption phenomenon is exothermic while a positive value implies that the adsorption process is endothermic. The magnitude and sign of ΔS^* gives an indication whether the adsorption reaction is an associative or dissociative mechanism. A negative value of ΔS^* suggests that the adsorption process involves an associative mechanism. The adsorption leads to order through the formation of an activated

complex between the adsorbate and adsorbent. Also a negative value of ΔS^* reflects that no significant change occurs in the internal structures of the adsorbent during the adsorption process. A positive value of ΔS^* suggests that the adsorption process involves a dissociative mechanism. Such adsorption phenomena are not favourable at high temperatures.

2.3 Thermodynamic parameters

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibb's free energy change, ΔG^0, is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Both enthalpy (ΔH^0) and entropy (ΔS^0) factors must be considered in order to determine the Gibb's free energy of the process. Reactions occur spontaneously at a given temperature if ΔG^0 is a negative quantity. The free energy of an adsorption process is related to the equilibrium constant by the classical Van't Hoff equation:

$$\Delta G^0 = -RT \ln K_D \tag{4}$$

where, ΔG^0 is the Gibb's free energy change (kJ. mol^{-1}), R is the ideal gas constant (8.314 J.mol^{-1}K^{-1}), and T is temperature (K) and K_D is the single point or linear sorption distribution coefficient defined as:

$$K_D = \frac{C_a}{C_e} \tag{5}$$

where C_a is the equilibrium adsorbate concentration on the adsorbent (mg L^{-1}) and C_e is the equilibrium adsorbate concentration in solution (mg L^{-1}).

Considering the relationship between ΔG^0 and K_D, change in equilibrium constant with temperature can be obtained in the differential form as follows

$$\frac{d \ln K_D}{dT} = \frac{\Delta H^0}{RT^2} \tag{6}$$

After integration, the integrated form of Eq. (5) becomes:

$$\ln K_D = -\frac{\Delta H^0}{RT} + Y \tag{7}$$

where Y is a constant.

Eq (7) can be rearranged to obtain:

$$-RT \ln K_D = \Delta H^0 - TRY \tag{8}$$

Let $\Delta S^0 = RY$

Substituting Eqs. (4) and (8), ΔG^0 can be expressed as:

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

A plot of Gibb's free energy change, ΔG^0 versus temperature, T will be linear with the slope and intercept giving the values of ΔH^0 and ΔS^0 respectively.

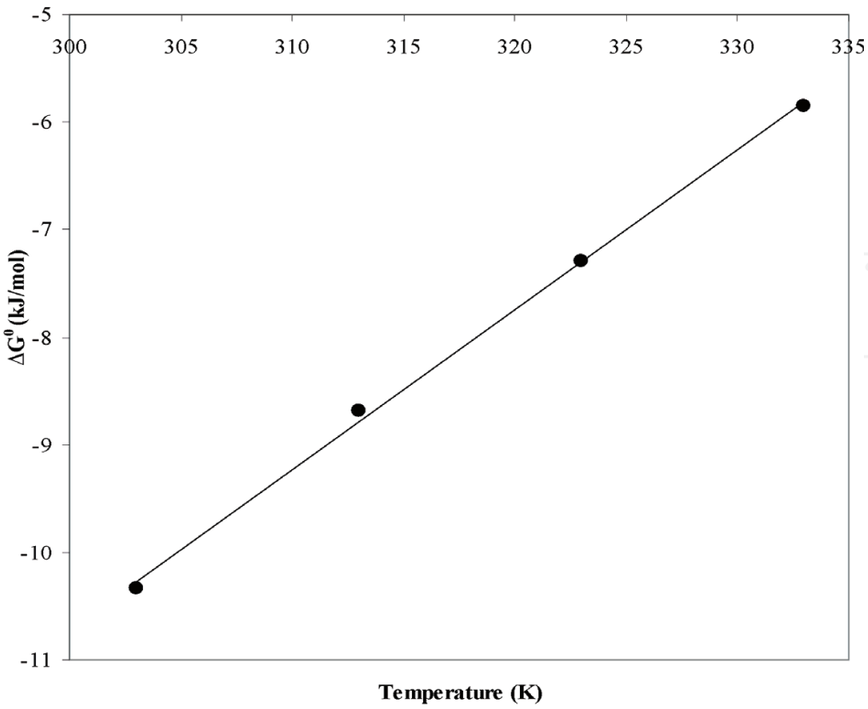


Fig. 3. Plot of Gibb's free energy change (ΔG^0) versus temperature for an exothermic process

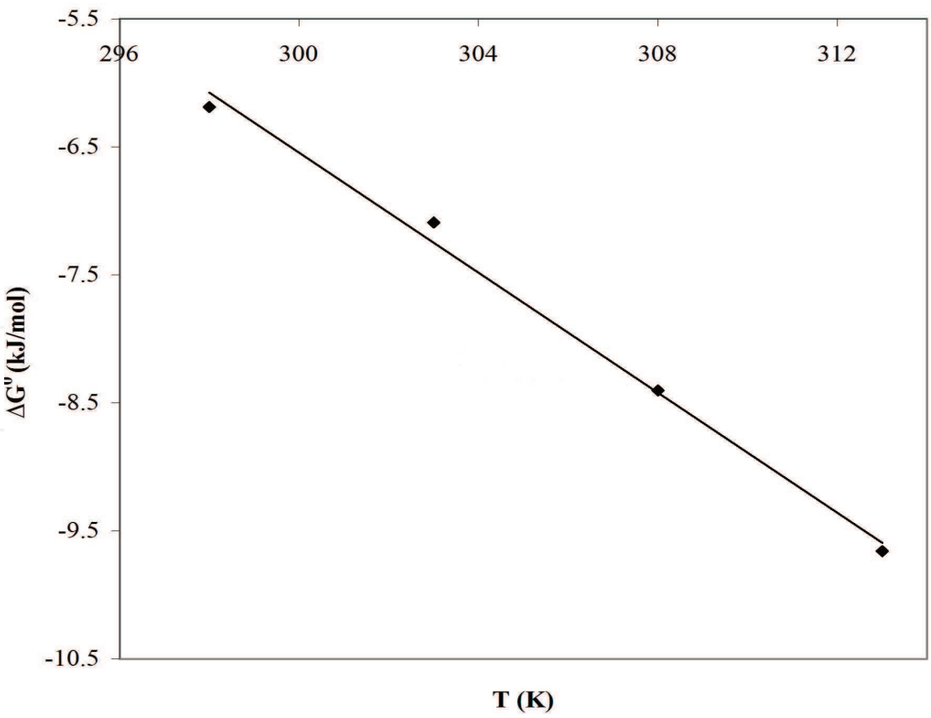


Fig. 4. Plot of Gibb's free energy change (ΔG^0) versus temperature for an endothermic process

The thermodynamic relation between ΔG^0, ΔH^0 and ΔS^0 suggests that either (i) ΔH^0 or ΔS^0 are positive and that the value of $T\Delta S^0$ is much larger than ΔH^0 (ii) ΔH^0 is negative and ΔS^0 is positive or (iii) ΔH^0 or ΔS^0 are negative and that the value of ΔH^0 is more than $T\Delta S^0$.
The typical value of the thermodynamic parameters for adsorption of heavy metal ions and synthetic dye molecules onto various low cost adsorbent are listed in Tables 2 and 3, respectively. For significant adsorption to occur, the Gibb's free energy change of adsorption, ΔG^0, must be negative. For example, as seen in Table 2, the Gibb's free energy change (ΔG^0) values were found to be negative below 313.15 K for adsorption of Cr(VI) onto chitosan, which indicates the feasibility and spontaneity of the adsorption process at temperatures below 313.15K. As a rule of thumb, a decrease in the negative value of ΔG^0 with an increase in temperature indicates that the adsorption process is more favourable at higher temperatures. This could be possible because the mobility of adsorbate ions/molecules in the solution increase with increase in temperature and that the affinity of adsorbate on the adsorbent is higher at high temperatures. On the contrary, an increase in the negative value of ΔG^0 with an increase in temperature implies that lower temperature makes the adsorption easier.

Adsorbent	**Adsorbate**	**T (K)**	**ΔG^0 (kJ mol^{-1})**	**ΔH^0 (kJ mol^{-1})**	**ΔS^0 (J mol^{-1})**	**Reference**
Rubber (*Hevea brasiliensis*) leaf powder	Cu(II)	300 310 320	-3.38 -2.17 -1.48	-31.96	-95.94	Ngah & Hanafiah, 2008
Modified oak sawdust	Cu(II)	293 303 313	-2.840 -3.064 -3.330	4.331	240	Argun et al., 2007
Mimosa tannin resin	Cu(II)	298 303 318 338 353	-2.47 -4.83 -8.51 -9.38 -11.45	42.09	153	Sengil & Ozacar, 2008
Hazelnut shell activated carbon	Cu(II)	293 303 313 323	-6.83 -6.66 -6.03 -5.71	18.77	40.4	Demribas et al., 2009
Penicillium simplicissimum	Cd(II)	293 303 313	-18.27 -19.81 -20.88	20.03	130.90	Fan et al., 2008
Red algae (*Ceramium virgatum*)	Cd(II)	293 303 313 323	-19.5 -19.0 -18.7 -18.2	-31.8	-42.4	Sari & Tuzen, 2008
Coconut copra meal	Cd(II)	299 311 323 333	-7.41 -7.15 -6.97 -6.66	-13.70	21.20	Ho & Ofomaja, 2006

Fennel biomass	Cd(II)	303 313 323	-5.017 -5.470 -6.016	10.34	51	Rao et al., 2010
Chitosan	Cr(VI)	303.15 313.15 323.15 333.15	-2.409 -1.326 0.178 2.429	-50.782	159	Aydin & Aksoy, 2009
Walnut hull	Cr(VI)	303 313 323	-23.03 -25.63 -28.77	64.14	287.4	Wang et al., 2009
Acacia leucocephala bark	Ni(II)	303 313 323	-6.147 -6.945 -7.847	10.389	55	Subbaiah et al., 2009
Baker's yeast	Ni(II)	300 313 323 333	-23.519 -23.408 -23.149 -22.708	-30.702	-23.658	Padmavathy, 2009
Oyster shell powder	Ni(II)	303 318 333	-20.0 -22.9 -26.4	44.90	127.7	Hsu, 2009
Lichen (*Cladonia furcata*) biomass	Ni(II)	293 303 313 323	-18.3 -14.4 -14.3 -14.4	-37.5	-71.5	Sari et al., 2009
Acacia leucocephala bark powder	Pb(II)	303 313 323	-3.876 -4.379 -4.997	-21.147	57	Munagapati et al., 2010
Penicillium simplicissimum	Pb(II)	293 303 313	-20.04 -22.60 -24.06	39.13	202.52	Fan et al., 2008
Lichen (*Cladonia furcata*) biomass	Pb(II)	293 303 313 323	-21.2 -17.4 -17.2 -17.1	-35.4	-57.6	Sari et al., 2009
Pine bark (*Pinus brutia* Ten.)	Pb(II)	273 283 293 303 313	-2.74 -2.89 -3.08 -3.25 -3.42	1.97	17.21	Gundogdu et al., 2009

Table 2. Thermodynamic parameters for adsorption of heavy metal ions on various low cost adsorbents

Adsorbent	**Adsorbate**	**T (K)**	**ΔG^0(kJ mol^{-1})**	**ΔH^0(kJ mol^{-1})**	**ΔS^0 (J mol^{-1})**	**Reference**
Treated ginger waste	Malachite Green	303 313 323	-1.515 -2.133 -3.016	47.491	167	Ahmad & Kumar, 2010
Degreased coffee bean	Malachite Green	298 308 318	-8.19 -10.0 -10.6	27.2	33.3	Baek et al., 2010
Neem sawdust	Malachite Green	298 308 318	-4.02 -2.33 -1.73	-54.56	-169.57	Khattri & Singh, 2009
Luffa cylindrical	Malachite Green	288 298 308	-6.1 -7.1 -8.7	32.1	132.2	Altınısık et al., 2010
Brazil nut shell	Methylene Blue	293 303 333	-2.27 -2.09 -1.97	-5.22	-112.23	Brito et al., 2010
Bentonite	Methylene Blue	283 293 303 308	-17.0 -17.7 -18.5 -19.4	9.21	92.2	Hong et al., 2009
Modified wheat straw	Methylene Blue	293 303 313	-9.96 -11.22 -12.14	21.92	108	Han et al., 2010
Cattail root	Congo Red	293 303 313	-7.871 -6.800 -4.702	-54.116	157	Hu et al., 2010
Ca-Bentonite	Congo Red	293 303 313 323	-6.4962 -6.7567 -7.1991 -11.179	5.1376	37.2	Lian et al., 2009
Non-living aerobic granular sludge	Acid Yellow 17	293 308 323	-5.14 -5.13 -4.65	-9.84	-15.79	Gao et al., 2010
P. vulgaris L. waste biomass	Reactive Red 198	293 303 313 323	-4.744 -4.573 -4.403 -4.232	-9.74	-17.04	Akar et al., 2009
Pinus sylvestris L. Biomass	Reactive Red 195	293 303 313 323	-13.253 -14.022 -15.723 -17.555	29.422	144.672	Aksakal & Ucun, 2010

Activated carbon from Brazilian-pine fruit shell	Reactive Orange 16	298 303 308 313 318 323	-32.9 -33.7 -34.6 -35.3 -36.2 -36.9	15.3	162	Calvete et al., 2010
Paulownia tomentosa Steud. leaf powder	Acid Orange 52	298 308 318	-0.85 -0.71 -0.51	-6.02	-17	Deniz & Saygideger, 2010
Brazil nut shell	Indigo carmine	293 303 333	-5.42 -5.71 -6.60	-3.20	-29.39	Brito et al., 2010
Activated carbon from bagasse pith	Rhodamine B	293 308 323 343	-7.939 -9.902 -12.361 -26.729	4.151	65.786	Gad & El-Sayed, 2009
Activated carbon from from *Euphorbia rigida*	Disperse Orange 25	283 288 293	-24.084 -25.736 -26.495	44.308	242.17	Gercel et al., 2008
Wheat bran	Astrazon Yellow 7GL	303 313 323	-14.472 -17.803 -22.552	46.81	175	Sulak et al., 2007

Table 3. Thermodynamic parameters for adsorption of synthetic dyes on various low cost adsorbents

A negative value of ΔH^0 implies that the adsorption phenomenon is exothermic while a positive value implies that the adsorption process is endothermic. The adsorption process in the solid–liquid system is a combination of two processes: (a) the desorption of the solvent (water) molecules previously adsorbed, and (b) the adsorption of the adsorbate species. In an endothermic process, the adsorbate species has to displace more than one water molecule for their adsorption and this result in the endothermicity of the adsorption process. Therefore ΔH^0 will be positive. In an exothermic process, the total energy absorbed in bond breaking is less than the total energy released in bond making between adsorbate and adsorbent, resulting in the release of extra energy in the form of heat. Therefore ΔH^0 will be negative. The magnitude of ΔH^0 may also give an idea about the type of sorption. The heat evolved during physical adsorption is of the same order of magnitude as the heats of condensation, i.e., 2.1–20.9 kJ mol^{-1}, while the heats of chemisorption generally falls into a range of 80–200 kJ mol^{-1}. Therefore, as seen from Tables 2 and 3, it seems that adsorption of most heavy metal ions and synthetic dye molecules by various low cost adsorbents can be attributed to a physico-chemical adsorption process rather than a pure physical or chemical adsorption process.

A positive value of ΔS^0 reflects the affinity of the adsorbent towards the adsorbate species. In addition, positive value of ΔS^0 suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent. The adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions/molecules, thus allowing for the prevalence of

randomness in the system. The positive ΔS^0 value also corresponds to an increase in the degree of freedom of the adsorbed species. A negative value of ΔS^0 suggests that the adsorption process is enthalpy driven. A negative value of entropy change (ΔS^0) also implies a decreased disorder at the solid/liquid interface during the adsorption process causing the adsorbate ions/molecules to escape from the solid phase to the liquid phase. Therefore, the amount of adsorbate that can be adsorbed will decrease.

2.4 Isosteric heat of adsorption

The most relevant thermodynamic variable to describe the heat effects during the adsorption process is the isosteric heat of adsorption. Isosteric heat of adsorption (ΔH_x, kJ mol^{-1}) is defined as the heat of adsorption determined at constant amount of adsorbate adsorbed. The isosteric heat of adsorption is a specific combined property of an adsorbent–adsorbate combination. It is one of the basic requirements for the characterization and optimization of an adsorption process and is a critical design variable in estimating the performance of an adsorptive separation process. It also gives some indication about the surface energetic heterogeneity. Knowledge of the heats of sorption is very important for equipment and process design. However, the physical meaning of 'isosteric heat' is not clear and it is not even considered by some authors to be the most suitable way of understanding the adsorption phenomena

The isosteric heat of adsorption at constant surface coverage is calculated using the Clausius-Clapeyron equation:

$$\frac{d(\ln C_{e)}}{dT} = -\frac{\Delta H_X}{RT^2} \tag{10}$$

where, C_e is the equilibrium adsorbate concentration in the solution (mg.L^{-1}), ΔH_x is the isosteric heat of adsorption (kJ mol^{-1}), R is the ideal gas constant (8.314 J.mol^{-1}K^{-1}), and T is temperature (K).

Integrating the above equation, assuming that the isosteric heat of adsorption is temperature independent, gives the following equation:

$$\ln C_e = -\left(\frac{\Delta H_X}{R}\right)\frac{1}{T} + K \tag{11}$$

where K is a constant.

The isosteric heat of adsorption is calculated from the slope of the plot of ln C_e versus $1/T$ different amounts of adsorbate onto adsorbent. For this purpose, the equilibrium concentration (C_e) at constant amount of adsorbate adsorbed is obtained from the adsorption isotherm data at different temperatures. The isosteres corresponding to different equilibrium adsorption uptake of Cu(II) by tamarind fruit seed is shown in Fig. 5. Similar isosteres have been obtained for other systems as well.

The magnitude of ΔH_x value gives information about the adsorption mechanism as chemical ion-exchange or physical sorption. For physical adsorption, ΔH_x should be below 80 kJ mol^{-1} and for chemical adsorption it ranges between 80 and 400 kJ.mol^{-1}.

The isosteric heat of adsorption can also provide some information about the degree of heterogeneity of the adsorbent. Generally, the variation of ΔH_x with surface loading is indicative of the fact that the adsorbent is having energitically heterogeneous surfaces. If it were a homogeneous surface, the isosteric heat of adsorption would have been constant

even with variation in surface loading. The ΔH_x is usually high at very low coverage and decreases steadily with an increase in q_e. The dependence of heat of adsorption with surface coverage is usually observed to display the adsorbent–adsorbate interaction followed by the adsorbate–adsorbate interaction. The decreasing of the heats of sorption indicates that the adsorbate–adsorbent interactions are strong in the range of lower q_e values and then they decrease with the increase in the surface coverage. It has been suggested that that the high values of the heats of sorption at low q_e values were due to the existence of highly active sites on the surface of the adsorbent. The adsorbent–adsorbate interaction takes place initially at lower q_e values resulting in high heats of adsorption. On the other hand, adsorbate–adsorbate interaction occurs with an increase in the surface coverage giving rise to lower heats of sorption. The variation in ΔH_x with surface loading can also be attributed to the possibility of having lateral interactions between the adsorbed adsorbate molecules.

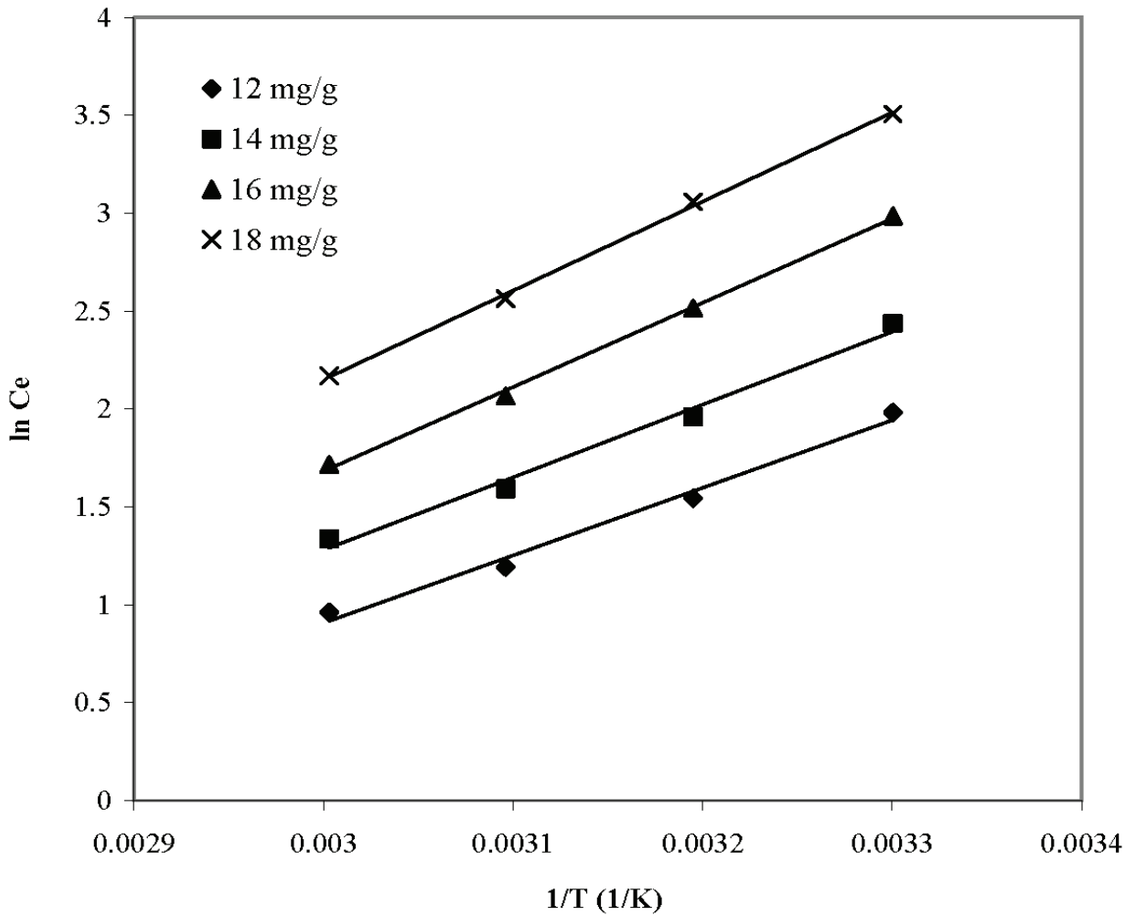


Fig. 5. Plots of ln C_e against 1/T for adsorption of Cu(II) onto tamarind seeds at constant surface coverage, q_e = 12, 14, 16, 18 mg g^{-1}

3. Conclusion

To date, adsorption has been regarded as an effective technology for the removal of soluble heavy metal ions, synthetic dye molecules and other toxic chemicals from aqueous solution.

In study of adsorption thermodynamics, it appears that determination of value of the thermodynamic quantities such as activation energy, activation parameters, Gibb's free energy change, enthalpy, entropy, and isosteric heat of adsorption are required. These parameters are critical design variables in estimating the performance and predicting the mechanism of an adsorption separation process and are also one of the basic requirements for the characterization and optimization of an adsorption process. So far, extensive research effort has been dedicated to a sound understanding of adsorption isotherm, kinetics and thermodynamics. Compared to adsorption isotherm and kinetics, there is lack of a theoretical basis behind the thermodynamic analysis of sorption data. In this regard, the next real challenge in the adsorption field is the identification and clarification of the underlying thermodynamics in various adsorption systems. Further explorations on developing in this area are recommended.

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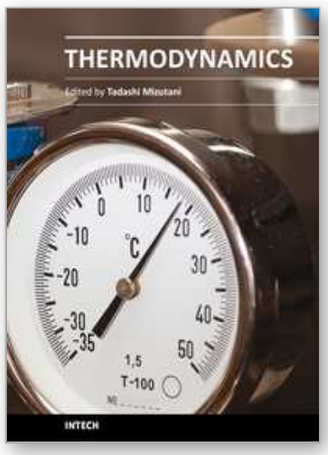
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