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A kinetic and thermodynamic study of cyanide adsorption in activated carbon

G.G. Stavropoulos*, M. Papadopoulou, K. Papadimitriou

Department of Chemical Engineering, Aristotle University of Thessaloniki, Univ. P.O. Box 1520, 54006, Thessaloniki, Greece, Tel. +30 2310 995918; Fax: +30 2310 996168; email: gstavrop@auth.gr (G.G. Stavropoulos)

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ABSTRACT

During last decades, cyanide adsorption has been studied in plain and in modified activated carbon, although the adsorption mechanism is not clarified. In this context, the investigation of adsorption energetics is of fundamental importance and can substantially contribute to understand the mechanism. In addition, determination of activation energies and adsorption and desorption constants are required in the modeling of adsorption and in the design and operation of adsorption equipment. For this purpose, the adsorption equilibrium and kinetics of cyanide adsorption in a commercial activated carbon were experimentally determined at various temperatures. By applying equilibrium and kinetics equations based on the Langmuir model, the respective constants were calculated i.e. equilibrium constant and adsorption and desorption kinetic constants. Calculation modality is not applied in literature yet. Further, by applying the classical Arrhenius methodology the pre-exponential factors and activation energies of adsorption and desorption were calculated. This procedure differs from that usually applied in the literature. It was found that CN^- is most probably hydrated and loosely adsorbed at room temperature. By increasing the temperature, hydration shield is destroyed and CN^- is adsorbed in a higher energy configuration.

Keywords: Activated carbon; Cyanide; Adsorption; Kinetics; Thermodynamics; Activation energies

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1. Introduction

Adsorption and more specifically adsorption in liquid phase have been extensively studied both experimentally and theoretically during last few years [1,2]. In a typical study, equilibrium, kinetic, and thermodynamic experimental data are acquired and interpreted with a number of theoretical models in order to calculate the respective constants and energies and to explore the adsorption mechanism [3]. Models are subsequently used for the design and operation of commercial adsorption equipment. In this regard, the effect of solution and adsorbent properties on adsorption is examined. Among these, concentration, solid load, pH, pH_{pzc}, temperature, and others are of interest. Special attention merits the effect of temperature on adsorption since it is correlated with the energy involved in the process. In the majority of studies, adsorption equilibrium data are modeled by the

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*Corresponding author.

Langmuir and Freundlich equations and kinetic data with pseudo-first and pseudo-second-order and other equations [4]. These models allow the calculation of the kinetic constants and the thermodynamic parameters of adsorption, namely: standard Enthalpy, Entropy, and Gibbs free energy making use of the Van't Hoff equation. Some researchers applied a different approach making use of the Langmuir theory of adsorption and the respective equilibrium and kinetic equations for the calculation of the equilibrium and kinetic constants and of the frequency factors and activation energies of the adsorption and desorption [5]. Calculations are based on some assumptions for the variation in the surface coverage with time. In the present work, no assumptions are made for the surface coverage variation during adsorption. This is simply the unknown problem and it is calculated from the experimental results, making use of Langmuir model equations. This procedure, not applied in any adsorption study yet, is used in cyanide adsorption. Cyanide is found in effluents from a number of industries and has attracted the attention of researches because of its toxic properties [6–9]. Despite these research efforts, the adsorption mechanism of cyanide in activated carbon is not elucidated and the present paper will contribute to this purpose.

2. Experimental

The adsorption experimental procedure is detailed elsewhere. One gram of activated carbon with code name D45/2 supplied by CarboTech, Essen, Germany, was admixed with 200 ml of cyanide solution of prescribed initial concentrations. Adsorbed amount was calculated by subtracting the initial concentration from the equilibrium dividing by carbon weight. Cyanide concentration was determined by the $AgNO_3$ titration method [10]. Equilibrium experiments were calculated at 24 h, time found to be sufficient in other experiments. Kinetic experiments were calculated by calculating adsorbed amounts at various time intervals, up to 24 h [4]. Experiments were conducted at temperatures between 20 and 60°C. Experiments were conducted at solution pH 10; a pH value found to be the optimum for maximum adsorption, considering the value of HCN $pK_a = 9.4$ and the $pH_{pzc} = 11$ of activated carbon [5]. pH values before and after the adsorption experiments did not changed appreciably. Therefore, adsorption was carried out at controlled pH values and consequently, controlled cyanide hydrolysis conditions were maintained at all concentrations and temperatures of the experiments.

3. Results and discussion

3.1. Equilibrium

The cyanide adsorption isotherms at temperatures between 20 and 60°C are seen in Fig. 1. Isotherms are modeled with the Langmuir equation:

$$\bar{C} = \bar{C}_m \frac{K C_e}{1 + K C_e} \tag{1}$$

where $\bar{C}_m$ = adsorbed amount at equilibrium (monolayer capacity of adsorbent) (mg/g), K = the equilibrium constant (l/mg), and C_e = equilibrium concentration (mg/l).

Correlation coefficients are high enough, demonstrating the suitability of the model for the experimental results. Model allows for the calculation of the adsorbed amount of cyanide at equilibrium and the equilibrium constant at each temperature, Table 1.

With increasing temperature equilibrium adsorbed amount of cyanide increases. This trend is characteristic of an endothermic process, although in the majority of cases, adsorption is exothermic.

3.2. Adsorption kinetics

The kinetic study is important for the adsorption process because it describes the rate of uptake of the adsorbate and controls the residence time of the adsorption equipment [3]. The kinetic model selected to describe the adsorption process in this study is the Langmuir model although in the literature the pseudo-first and pseudo-second-order kinetic models are applied. The reason is that the Langmuir model, if applied to the experimental results, is a well-

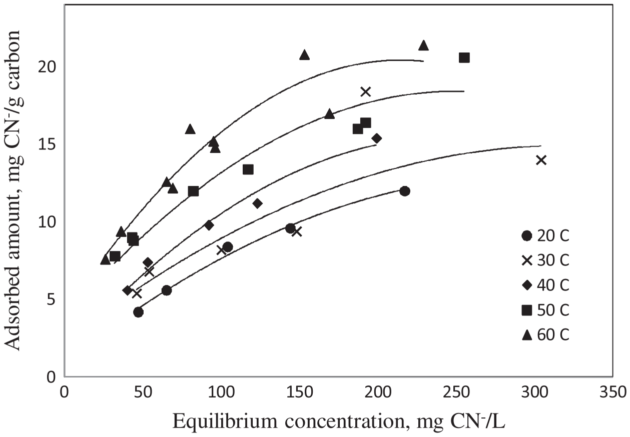

Fig. 1. Adsorption isotherms at various temperatures.

Table 1
Equilibrium constants at various temperatures

T (C)	20	30	40	50	60
$\bar{C}_{\mathrm{m}}$	23.8	21.5	25.9	24.8	27.3
$K \times 10^{-3}$ (1/mg)	4.7	7.4	6.8	12.0	13.7
R^2	0.997	0.999	0.994	0.953	0.915

documented model that allows for the calculation of equilibrium and kinetic constants. To the best of our knowledge, the calculation modality adopted here is not yet applied in the literature.

3.2.1. Model application and validation

Langmuir model is based on the reaction mechanism: $A + X \leftrightarrow AX$, and on the respective kinetic equation:

$$r = \frac{\mathrm{d}\bar{C}}{\mathrm{d}t} = k\,C\,\bar{C}_{\mathrm{v}} - k'\,\bar{C} \tag{2}$$

where $\bar{C}$ = adsorbed amount of adsorbent (mg/g), C = concentration in liquid phase of adsorbent (mg/l), $\bar{C}_{\mathrm{v}}$ = concentration of the vacant sites for adsorption (mg/g) adsorbent, t = contact time for adsorption (h), k = adsorption constant (1/h mg), k' = desorption constant (h^{-1}) and using calculated values $\bar{C}_{\mathrm{m}}$ and K from isotherms, Table 1, the values of k and k' are calculated from the equations:

$$k = \frac{1}{t}\int_0^{\bar{C}} \frac{\mathrm{d}\bar{C}}{\bar{C}^2\left(\bar{C}_{\mathrm{m}} + C_0 + \frac{1}{K}\right)\bar{C} + \bar{C}_{\mathrm{m}}C_0} \tag{3}$$

$$k' = \frac{k}{K} \tag{4}$$

The detailed procedure can be found elsewhere [4]. In Table 2, calculated values of the adsorption constants are reported at temperatures between 20 and 60°C.

Table 2
Adsorption–desorption kinetic constants at various temperatures

T (°C)	20	30	40	50	60
$k \times 10^{-4}$ (l/h mg)	4.65	4.70	5.55	4.52	5.11
$k' \times 10^{-2}$ (h^{-1})	9.79	6.29	8.07	3.76	3.71

3.2.2. Predictive potential of the model

Once the kinetic constants have been calculated they can be used to predict the adsorption at different initial concentrations, C_0. The procedure makes use of Eq. (2). By introducing estimated values of k and k', it can be calculated the time t required to obtain an adsorbed amount $\bar{C}$ of cyanide:

$$t = \int_0^t dt = \int_0^{\bar{C}} \frac{\mathrm{d}\bar{C}}{a\bar{C}^2 + b\bar{C} + c} \tag{5}$$

where $a = k$, $b = -(\mathrm{k}\bar{C}_{\mathrm{m}} + kC_0 + k')$, $c = k\bar{C}_{\mathrm{m}}C_0$.

Model fits the experimental results quite satisfactorily, as can be concluded from Fig. 2.

3.3. Activation energies—adsorption mechanism

In a next step, the adsorption–desorption frequency factors k_0 and k'_0 and the activation energies E_0, E'_0 can be readily calculated from the linear form of Arrhenius equation [11].

The Arrhenius equations for sorption and desorption are given below:

$$k = k_0 e^{-E_0/RT} \tag{6}$$

$$k' = k'_0 e^{-E'_0/RT} \tag{7}$$

where E_0, E'_0 = the activation energies of adsorption and desorption, respectively (kcal/mol), k_0, k'_0 = frequency factors, R = universal gas constant, and T = absolute temperature (K).

Eqs. (6) and (7) are used in their linear form:

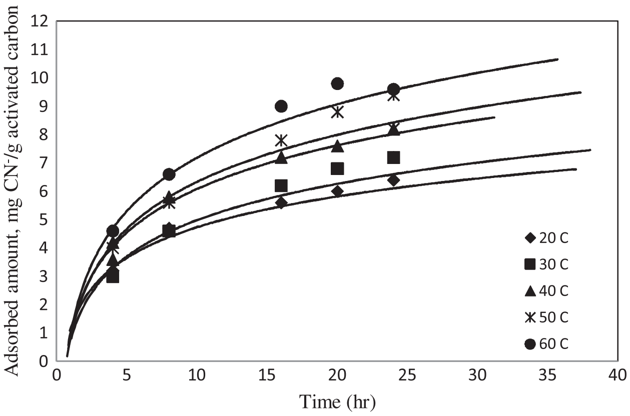

Fig. 2. Kinetic modeling of cyanide adsorption. Points: experimental results and curves: model results.

$$\ln k = \ln k_0 - \frac{E_0}{R}\frac{1}{T} \tag{8}$$

$$\ln k' = \ln k'_0 - \frac{E_0}{R}\frac{1}{T} \tag{9}$$

The frequency factors and the activation energies can be calculated from the slope and the intercept on the plot of ln k vs. $1/T$, according to the linear equation of Arrhenius as shown in Fig. 3. The numerical results are presented in Table 3.

Adsorption activation energy is quite low. Desorption activation energy is higher, although in the order of magnitude of physisorption. At low temperature, the cyanide is hydrated and it is adsorbed loosely in the diffuse layer of the electrical double layer. Adsorption energy is low, since adsorption (electrostatic) interactions between carbon positive charges and cyanide is "not strong" due to the water molecules shield between carbon surface and cyanide ion. By increasing temperature, energy is supplied to the system, enough to remove and exchange the solvation sheath around the cyanide ion. This is the most probable explanation given also by other researchers. The amount of energy is quite low, 0.29 kcal/mol, equal to the activation energy calculated for adsorption (Table 3). Generally, increase in adsorption with temperature has been encountered in a number of works. The usual explanation is that although adsorption is exothermic, the dehydration process that precedes adsorption is endothermic. The enthalpy of the later is higher than that of the former and the overall process results endothermic. In parallel, the overall equilibrium constant is affected by the kinetics of dehydration. Since K of adsorption is expected to decrease with temperature, the kinetic constant of dehydration increases sufficiently to overcome the decrease of K. In order to further elucidate the adsorption mechanism of cyanide on carbon surface, the adsorbent–adsorbate bond must be investigated experimentally using techniques such as SEM, FTIR, and XPS. Experiments are under way and results would be published in an upcoming paper.

Table 3
Pre-exponential factors and activation energies of cyanide adsorption–desorption

$k_0 \times 10^{-4}$	$k'_0 \times 10^{-5}$	E_0 (kcal/mol)	E'_0 (kcal/mol)
7.87	2.81	0.29	4.74

3.4. Thermodynamics

The concept of thermodynamics assumes that in an isolated system where energy cannot gain or lost, the entropy change is the driving force [5]. Gibbs free energy is the chemical potential that is minimized when the system reaches equilibrium at constant temperature and pressure and is calculated using the equation below:

$$\Delta G^\circ = -RT \ln K_{eq} \tag{10}$$

where K_{eq} = adsorption equilibrium constant (calculated from the Langmuir isotherm), T = absolute temperature (K), and R = universal gas constant (kcal/mol K).

Substituting the change in Gibb's free energy and solving Eq. (10) for the natural log results in the linear form of the Van't Hoff's equation:

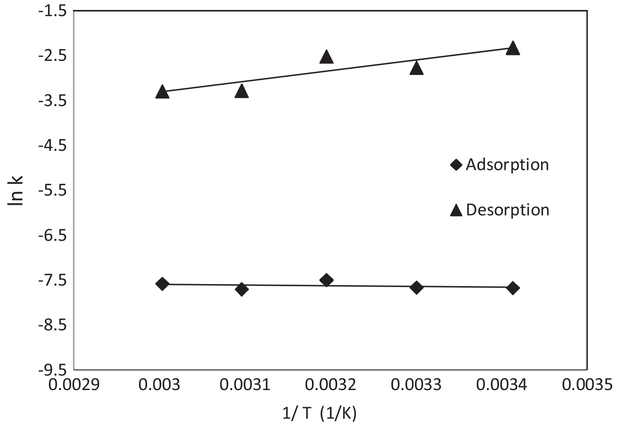

Fig. 3. Arrhenius plot for adsorption and desorption of cyanide onto activated carbon.

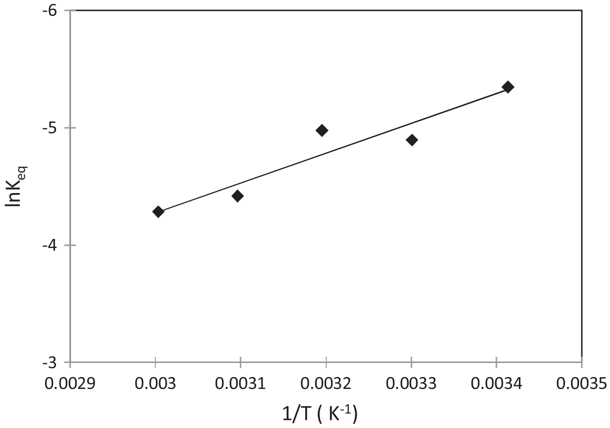

Fig. 4. Van't Hoff plot.

Table 4
Thermodynamic parameters of cyanide adsorption in activated carbon D45/2

T (°C)	K_{eq} (1/mol)	ΔG° (kJ/mol)	ΔH°	ΔS°
20	122	–11,7026		
30	192	–13,2444		
40	176	–13,4551	21.292 kJ/mol	0.1128 kJ/mol K
50	312	–15,4224	5.323 kcal/mol	0.0282 kcal/mol
60	356	–16,2651		

$$\ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{11}$$

The thermodynamic parameters ΔH° and ΔS° can be calculated from the slope and the intercept of the plot: $\ln K_{eq}$ vs. $1/T$, according to the equation of Van't Hoff Eq. (11), (Fig. 4). The numerical results are shown in Table 4.

The Gibbs free energy change is negative demonstrating that adsorption is spontaneous under the experimental conditions applied. The absolute values are increasing with temperature indicating a more favorable process at higher temperatures.

The positive values of standard enthalpy of adsorption indicates an endothermic process, a conclusion already found and justified earlier. Finally, the positive and low value of ΔS° suggests some minor structural changes in the adsorbent after adsorption.

4. Conclusion

The adsorption of cyanide onto activated carbon was studied experimentally and theoretically in this work. The effect of temperature on adsorption was of major concern. Kinetics and equilibrium experimental results were fitted with the Langmuir model resulting in the calculation of respective constants and activation energies. Thermodynamic parameters were estimated with the usual methodology (Van't Hoff equation). Adsorption was shown to increase with temperature showing an overall endothermic process requiring energy to occur. Activation energies involved were low indicating a weak physisorption mechanism. Energy is required to dehydrate cyanide ion and therefore increase adsorption. The low adsorption capacity of carbon together with the low energetics and the values of thermodynamic parameters indicate a weak adsorption mechanism between cyanide and plain carbon, which seem not to be the best choice for CN^- adsorption. Carbon surface modifications that will increase adsorbing capacity can, for instance, be applied in order to obtain a technically and economically viable adsorbent.

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