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Effects of Biodegradation and Background Inorganic Substances on Granular Activated Carbon Adsorption of Wastewater

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ABSTRACT

Background inorganic substances are thought to disrupt the adsorption process used in wastewater treatment systems. In this study, a low-strength synthetic wastewater was investigated for biodegradation and adsorption onto granular activated carbon, with and without the presence of background inorganic compounds. Overall, organic compounds in the synthetic wastewater underwent slow biodegradation, but when a solution was prepared with only one or two individual organic components present in the wastewater, biodegradation ceased. This effect was noticed both in

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the presence and absence of inorganic compounds. The association theory was found to describe the overall adsorption equilibrium of the system better than the more commonly used Freundlich isotherm. The isotherm patterns of the synthetic wastewater indicated that the dissolved inorganic substances had unfavorable effects on the adsorption of dissolved organic substances.

Key Words: Adsorption isotherm; Association theory; Granular activated carbon; Organic concentration; Total organic carbon; Synthetic wastewater.

INTRODUCTION

The adsorption of organics from wastewater is a very complex phenomenon. Wastewater contains so many different organic and inorganic compounds, it is not feasible to identify and quantify them all. Each of these compounds may influence the adsorption of others, since they compete with one another for adsorption. Depending on the characteristics of adsorbates and adsorbents, and the subsequent interaction among themselves, the nature and shape of the adsorption curves change. It is, therefore, important to evaluate the effect of interactions between the dissolved substances to determine the capacity of the adsorbent, and to model the adsorption system. Since, the first step in designing an adsorption system is to determine the equilibrium isotherm of the adsorbate–adsorbent system, precise determination of the equilibrium isotherm parameters using a suitable isotherm model is very important. However, the equilibrium isotherm of an adsorbate–adsorbent system is influenced by many factors, such as pH, temperature, organic, and inorganic contents. Weber et al.[1] observed a substantial increase in the adsorption of humic substances by activated carbon with increasing Ca^{2+} ion concentration. The effects of Mg^{2+}, K^{+}, and Na^{+} ions were also found favorable for adsorbing humic substances. Inorganic compounds also display a wide range of adsorbability.[2] Sodium chloride, a strongly dissociated inorganic compound, is essentially not adsorbed by activated carbon, whereas the nondissociating inorganic compound iodine chloride is readily adsorbed onto activated carbon. Similarly, hydroxyl, amino, and sulphonic substituent groups were found to decrease the adsorbability of the solution, whereas nitro groups often enhanced adsorption activity.[3] Snoeyink et al.[4] reported a significant increase in adsorption of p-nitrophenol to, activated carbon when NaCl was added at pH 10 (at which p-nitrophenol is fully ionized), whereas at pH 2 (at which the p-nitrophenol is not iodized at all), there was no effect. Similarly, $CaCl_2$ was also found to improve the adsorption of sodium benzene sulphonate.[5] Cooney and Wijaya[6] observed that the addition of NaCl significantly increased the adsorption of various organic compounds such as benzoic acid, aniline, m-phenylenediamine, and anthranillic acid when pH was maintained to keep these compounds in an ionized state.

In this study, seven inorganic and three organic compounds were used in the preparation of the synthetic wastewater, so it is worthwhile to discuss the overall effect of inorganic compounds on the isotherm pattern of the wastewater adsorption system. The effect of organic compounds on the isotherm is not discussed, because its adsorption is represented in terms of the total organic carbon (TOC). The main objective of this study was (1) to evaluate the biodegradable and adsorbable fractions of organics in the wastewater, (2) to determine the overall effect of the dissolved inorganic substances on adsorption, and (3) to find out the effect of initial organic concentration on the adsorption isotherm. The widely used Freundlich isotherm was also compared with the isotherm described by the association theory.[7]

ADSORPTION EQUILIBRIUM

When an amount of adsorbent comes into contact with a given volume of a solution containing an adsorbable solute (adsorbate), the adsorption phenomenon occurs until equilibrium is reached. The state of equilibrium is characterized by an adsorbed solute concentration in the adsorbent, and the resulting equilibrium solute concentration in the liquid phase. These relationships for a range of concentrations at constant temperature are called adsorption isotherms. Equation 1 is the most fundamental representation of an adsorption isotherm. Precise description of the adsorption equilibrium by an appropriate isotherm equation is the primary step in the design of an adsorption system as it reflects the capacity or affinity of an adsorbent for a particular adsorbate.

$$q = f(C), T = \text{constant} \tag{1}$$

Where, $q =$ amount adsorbed per unit mass of adsorbent, $C =$ concentration of the adsorbate in the solution, and $T =$ temperature.

Several adsorption isotherms are reported in published research results. The Freundlich isotherm is widely used as an empirical equation for qualitative purposes in both single component and multicomponent adsorption systems. The Freundlich isotherm is based on the assumption that there is no association or dissociation of the molecules after they are adsorbed on the surface and chemisorption is completely absent. However, in the Freundlich isotherm, the amount adsorbed increases infinitely with the increase in concentration, which is unrealistic and this greatly limits the usefulness of the Freundlich isotherm in describing the isotherm results over a wide range of concentrations.

In a multicomponent adsorption system, the isotherm equation becomes very complex due to the interactions between different adsorbate components and competitive adsorption interactions. The ideal adsorbed solution theory (IAST) first developed by Myers and Prausnitz[8] for gas mixtures is the most commonly used expression for isotherms in multicomponent adsorption history. It is based on the theory of adsorption thermodynamics, and since the extension of the theory to multicomponent liquid phase adsorption by Radke and Prausnitz,[9] most researchers have used this theory along with the Freundlich isotherm to describe the multicomponent isotherm results.[10,11] The IAST theory is based on the assumption that adsorption takes place at constant temperature and that the same adsorbent site is available for all adsorbates.

In this study, the association theory proposed by Talu and Meunier[7] was used to describe the overall adsorption isotherm. Talu and Meunier[7] first proposed this theory to better understand water vapor adsorption on hydrophobic surfaces, especially on activated carbon. The association theory takes into account three main characteristics of the adsorption system: chemical equilibria, equation of state, and phase equilibrium. Here, chemical equilibria and equation of state describe the behavior of the surface phase, and the phase equilibrium links the surface phase properties to bulk phase properties. The theory assumes that (1) primarily organic adsorption takes place on the active sites of the granular activated carbon (GAC) surface, (2) dissolved organic molecules form clusters around these sites by association, and (3) the adsorption site is limited by micropore volume irrespective of the shape and size of the micropores. Talu and Meunier[7] derived a set of equations for chemical equilibria, surface phase equation of state, and phase equilibria, and combined all these equations to derive the following three simplified equations to describe the overall adsorption isotherm. The details of the equations are given elsewhere.[7] The terms used in these equations here have been redefined to best describe the adsorption isotherm characteristics of the wastewater.

$$C_e = \frac{H\Psi \cdot \exp\left(\frac{\Psi}{q_e}\right)}{(1 + K\Psi)} \tag{2}$$

$$\Psi = \left(\frac{-1 + (1 + 4K\zeta)^{0.5}}{2K}\right) \tag{3}$$

$$\zeta = \frac{q_e q}{q_e - q} = \Psi(1 + K\Psi) \tag{4}$$

Where, $C_e =$ equilibrium organic concentration, mg/L, $H =$ adsorption constant (Henry's law), $K =$ reaction constant, $q_e = q_m =$ saturation amount of organic adsorbed, mg/g, $\psi =$ organic concentration spreading parameter, and $q =$ measured amount of organic adsorbed, mg/g.

The main reason for utilizing this theory was the unfavorable nature of the isotherm curves in a wide range of initial organic concentrations in the wastewater (3 to 12 mg/L of TOC). The theory has been tested in this study for the wastewater adsorption system. The theory is very simple and the required parameters (C_e and q) to describe the adsorption isotherm can be obtained from a simple integral adsorption equilibrium test in the laboratory as shown in Eq. (5).

$$q_e = (C_e - C_0)\frac{V}{M} \tag{5}$$

Where, $C_0 =$ initial organic concentration, mg/L, V = volume of the solution used in the equilibrium test, L, and M = weight of the activated carbon used in the equilibrium test, g.

The Freundlich isotherm, eq. (6), was also used to compare the results with the association theory.

$$q_e = kC_e^{1/n} \tag{6}$$

Where, k and n are Freundlich adsorption and exponential constants.

MATERIALS AND METHODS

Seven inorganic and three organic compounds were used to prepare the synthetic wastewater solution. The chemical composition of the synthetic wastewater used is shown in Table 1. This composition of the wastewater was

Table 1. Constituents of the synthetic wastewater.

Compounds	Weight (mg/L)	Compounds	Weight (mg/L)
$MnSO_4$	0.125	KH_2PO_4	1.250
$CaCl_2$	0.925	$NH_2 \cdot NH_2 \cdot H_2SO_4$	3.500
$NaHCO_3$	0.875	Glucose	16.500
NaCl	2.500	Yeast extract	1.750
$MgSO_4 \cdot 7H_2O$	3.750	Peptone	1.750

also used by the previous researcher.[12,13] Here, the TOC contribution of the organics, glucose, peptone, and yeast extract with inorganics are 79%, 11%, and 10%, respectively. In terms of TOC level, this synthetic wastewater composition represents a well-treated secondary effluent from a biological wastewater treatment plant (TOC = 3.5 mg/L and COD = 30 mg/L).

The physical properties of the granular activated carbon (GAC) used as adsorbent are shown in Table 2. Isotherm experiments were conducted using 250 mL of the synthetic wastewater solution in flasks. The amount of GAC varied from 0.003 g to 3 g. The flasks were shaken continuously for 7 days at 130 rpm at 25°C. Three different initial organic concentrations (of TOC) for the synthetic wastewater were used to evaluate the effect of initial organic concentration on isotherm parameters. Isotherm experiments involving synthetic wastewater with individual organic component and binary organic component systems, with and without inorganic compounds, were also carried out to evaluate the effect of inorganics and competitive organic substances on adsorption. Prior to the isotherm experiments, detailed studies were carried out of the biodegradation of the organics in the synthetic wastewater.

Table 2. Physical properties of GAC used.

Specification of the GAC	Estimated value
Iodine number, mg/(g.min)	800
Maximum ash content, %	5
Maximum moisture content, %	5
Bulk density, kg/m^3	748
BET surface area, m^2/g	1112
Nominal size, m	3×10^{-4}
Average pore diameter,Å	26.14

The effect of biodegradation was incorporated into the calculation of isotherm parameters. One blank wastewater solution was kept in the isotherm test. The equilibrium-adsorbed values were calculated based on the value of the blank solution (not the initial value of TOC of the wastewater). All the experiments were carried out at room temperature.

Total organic carbon (TOC) was measured using the UV-persulphate TOC analyzer (Dohrmann, Phoenix 8000, USA). The GAC used in the experiments was first washed three times with distilled water and dried in the oven at 103.5° C for 24 hours. It was kept in a desiccator before use in the experiments.

RESULTS AND DISCUSSION

The results of the biodegradation studies, and the adsorption equilibrium studies of the individual organic components, binary mixtures, and the overall synthetic wastewater with and without inorganic compounds are discussed in the following sections.

Biodegradation of Organics

Wastewater contains a complex matrix of organic and inorganic substances. The biodegradation of organics in the wastewater needs to be analyzed first to describe adsorption phenomenon with precision. It is necessary to differentiate between biodegradable and adsorbable portions of organics while determining the overall adsorption isotherm of the wastewater. Detailed experiments were conducted to determine the biodegradation rate of the organic compounds in the synthetic wastewater. Biodegradation of individual organics (glucose, peptone, and yeast extract) with and without the inorganics (see Table 1) was not substantial for 24 hours (Figs. 1 and 2). The biodegradation of the binary solution of these organics with the inorganics was also not significant (Fig. 3). However, the mixture of these organics with and without the inorganics was found to exhibit mild degradation in the first 8 hours and significant biodegradation after 10 hours (Fig. 4). It was further observed that biodegradation of the mixture of these organics was enhanced in the presence of inorganic compounds. This may be due to the abundant supply of nutrients from these inorganic substances.

Assuming a first-order biodegradation reaction, the average reaction rates for the synthetic wastewater with and without inorganics were calculated to be 0.0178

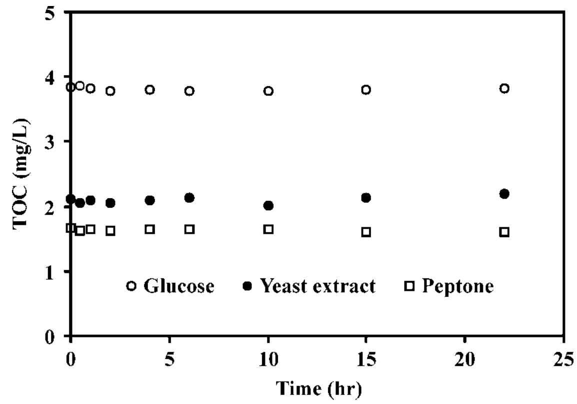

Figure 1. Biodegradation of the individual component of the synthetic wastewater without inorganics.

1/h, and 0.0073 1/h, respectively. The biodegradation of the organics was further investigated at different initial organic concentrations of the synthetic wastewater as well as under dynamic conditions using a simple mechanical stirrer. The biodegradation rate was found to decrease depending on the initial organic concentration of the solution, whereas no change in the degradation rate was observed when the solution was allowed to degrade under dynamic conditions (mixing speed 100 rpm).

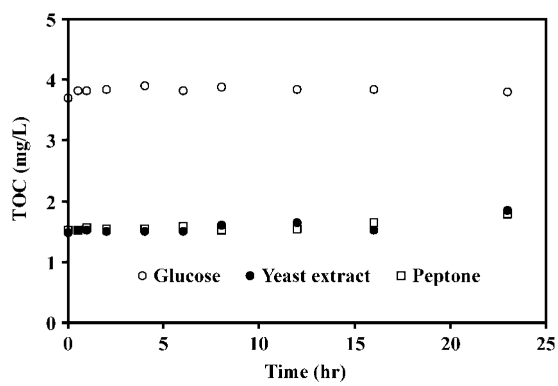

Figure 2. Biodegradation of the individual component of the synthetic wastewater with inorganics.

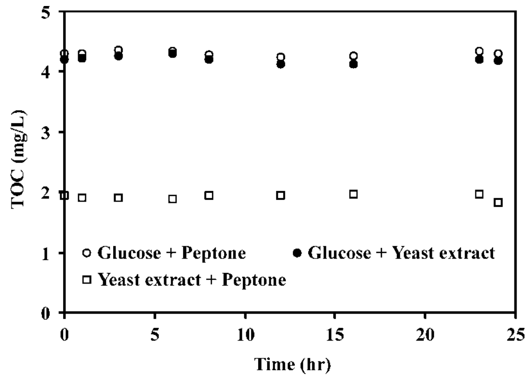

Figure 3. Biodegradation of the binary solution of the organics of the synthetic wastewater with inorganics.

The biodegradation of organics in the synthetic wastewater was not influenced by whether it took place under static or dynamic conditions. The biodegradation rate of synthetic wastewater at different organic concentrations is given in Table 3. A small dose (1 mg/L) of silver sulfate ($AgSO_4$) was found to retard the biodegradation rate for a few hours only. However, the silver sulfate solution was not used in this study to avoid possible interference with the solution on adsorption process.

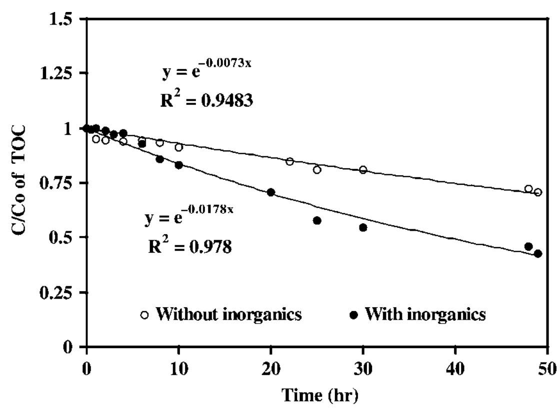

Figure 4. Biodegradation of the synthetic wastewater with and without inorganics.

Table 3. Biodegradation rate of synthetic wastewater at different organic concentrations.

Initial organic concentration (mg/L)	Biodegradation rate (L/h)
2.89	0.08
4.09	0.0164
8.20	0.015
11.35	0.0071
18.56	0.0063

Effects of Inorganics on the Overall Adsorption Isotherm

The isotherm experimental results for the synthetic wastewater, and the individual organic component of the synthetic wastewater, with and without inorganic substances, revealed that the overall effect of presence of the inorganic compounds used in the preparation of the synthetic wastewater did not favor the adsorption of the organics (Figs. 5 through 8). Due to the presence of inorganic compounds, the isotherm curve was found to shift toward the right, thus increasing the value of equilibrium concentration. It clearly indicated that the presence of inorganic compounds has an unfavorable

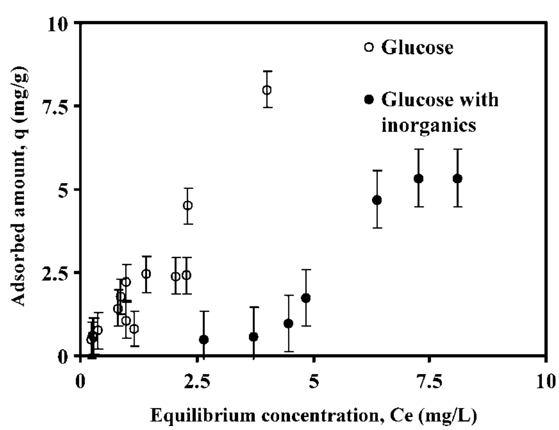

Figure 5. Equilibrium isotherm of glucose with and without inorganics.

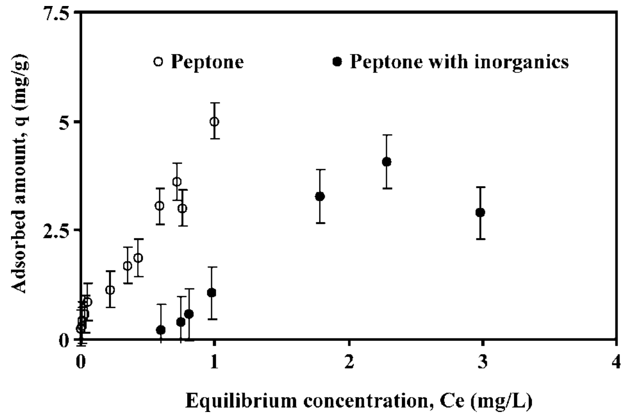

Figure 6. Equilibrium isotherm of peptone with and without inorganics.

effect on the adsorption characteristics of the organics. This could be due to the fact that part of the inorganic compounds in the solution were adsorbed onto the GAC surface, so reducing the available adsorption sites for organic compounds. As a result, the equilibrium total organic concentration in the bulk phase is higher in cases where inorganic substances are present in the solution.

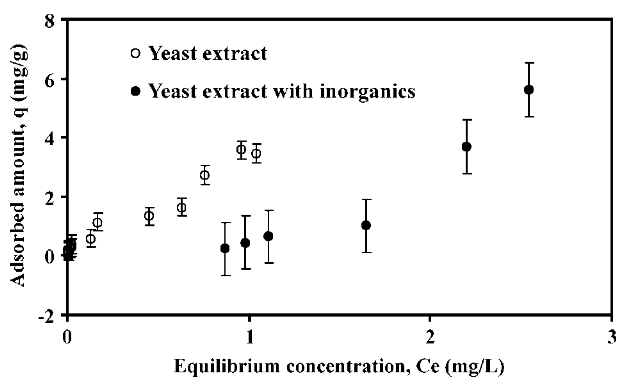

Figure 7. Equilibrium isotherm of yeast extract with and without inorganics.

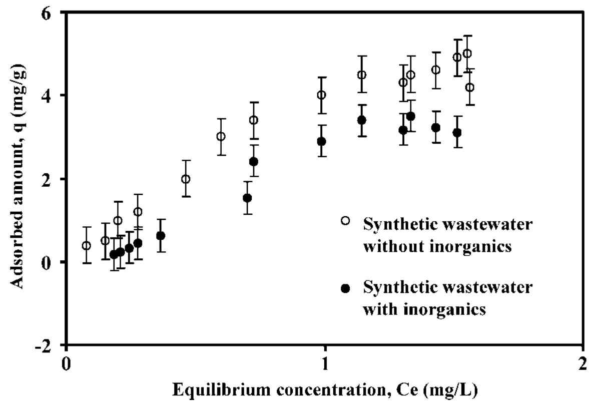

Figure 8. Overall adsorption isotherm of the synthetic wastewater with and without inorganics.

Effects of Initial Organic Concentration on the Adsorption Isotherm Parameters

The overall adsorption isotherm studies were carried out at different initial total organic concentrations (TOC) of the synthetic wastewater with inorganics. As mentioned earlier, the isotherm parameters were determined using the association theory proposed by Talu and Meunier.[7] The more

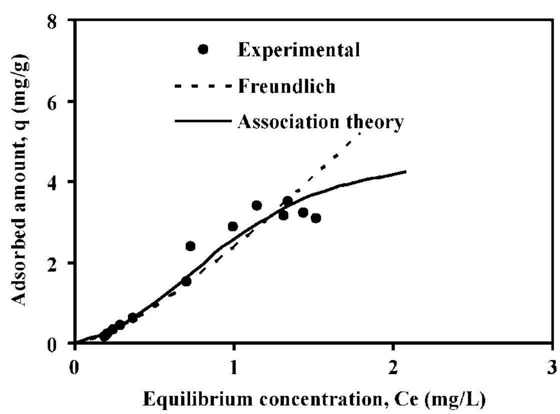

Figure 9. Overall adsorption isotherm at initial TOC concentration of 3.5 mg/L.

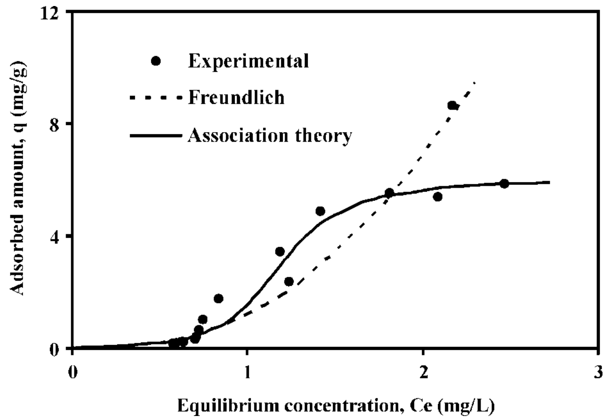

Figure 10. Overall adsorption isotherm at initial TOC concentration of 6.4 mg/L.

commonly used Freundlich isotherm was also used to compare the results with the association theory. As can be seen from Figs. 9 through 11(Table 4), the association theory was found to fit better with the experimental results than the Freundlich isotherm. Yuasa et al[14] also reported that the overall adsorption equilibrium of a multicomponent system could not be described well by Freundlich isotherm alone. Figure 12 shows the effect of initial organic

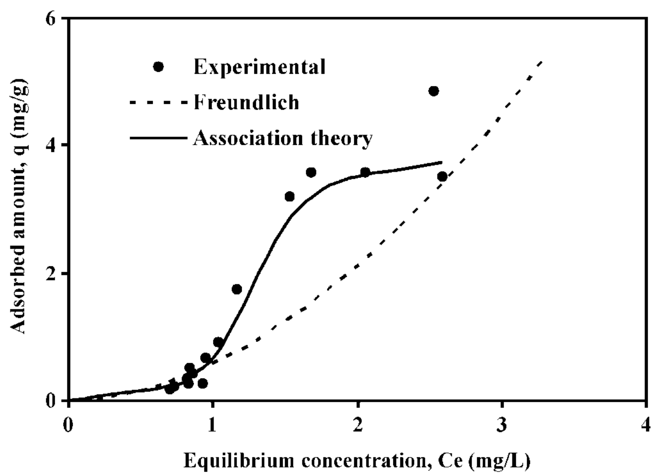

Figure 11. Overall adsorption isotherm at initial TOC concentration of 11.2 mg/L.

Table 4. Isotherm parameters and percent error of prediction.

Initial TOC of synthetic wastewater(mg/L)	Association theory				Freundlich isotherm		
	q_m	K	H	Error %	k	1/n	Error %
3.5	5.28	0.85	0.95	1.16	2.36	1.38	1.31
6.4	6.12	5.95	7.24	1.71	1.19	2.54	3.18
11.2	3.93	10.20	13.5	2.50	0.57	1.87	3.94

concentration on the isotherm parameters. This study indicates that the isotherm parameters are highly dependent on the initial concentration of organics in the wastewater and, therefore, it is important to obtain isotherm parameters covering a wide range of initial organic concentrations. The dependency of the isotherm parameters on the initial adsorbate concentration was reported to be due to the heterogeneous nature of the background compounds.[14–17] Matsui et al[11] also found that the initial organic concentration had a significant effect on the isotherm curve. The isotherm parameters of the equilibrium study on the synthetic wastewater system and the percent error of prediction are presented in Table 4.

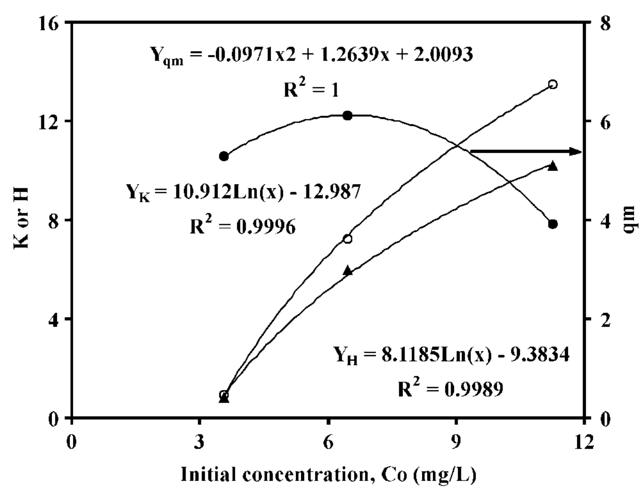

Figure 12. Effect of initial TOC concentration on isotherm parameters of the association theory.

CONCLUSION

The following conclusions were drawn from this study.

1. In a multicomponent adsorption system, such as adsorption of organics from wastewater by GAC, where biodegradation of the organics is also most likely to occur, the biodegradable and adsorbable organic fractions should be differentiated while determining the adsorption equilibrium parameters.
2. The state of the adsorption equilibrium depends on the initial adsorbate concentration. Therefore, the isotherm parameters should be determined covering a wide range of initial adsorbate (organic) concentrations.
3. Background inorganic substances can influence the adsorption behavior of organics (present in wastewater) on GAC. In this study, the overall effect of the inorganics present in the synthetic wastewater was unfavorable for the adsorption of organics.
4. Overall, organic compounds in the synthetic wastewater underwent a slow biodegradation but when a solution was prepared with one or two individual organic components present in the wastewater, it did not exhibit any biodegradation.
5. The association theory was found to describe the adsorption equilibrium of the synthetic wastewater better than the more commonly used Freundlich isotherm. The association theory was found to be more efficient in predicting the isotherm results within the TOC range studied.

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