



Equilibrium and Thermodynamic Studies for Adsorption of 1,4-Benzoquinone by Fly Ash

Guoting Li†, Yanmin Feng, Xiaoqi Chai and Xiaoshuang He

Department of Environmental and Municipal Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450011, P.R. China

†Corresponding author: Guoting Li

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ABSTRACT

Fly ash, an industrial waste from thermal power plants, was used for the adsorptive removal of 1,4-benzoquinone, one of the oxidation intermediates generated in AOPs. Effect of fly ash dosage and solution pH was investigated. The highest 1,4-benzoquinone uptake occurred at pH 7.0. Neutral and alkaline conditions were more favourable for the adsorptive removal of 1,4-benzoquinone. Isotherm data at 288, 298 and 308 K were simulated by Langmuir, Freundlich, Temkin, Redlich-Peterson, Koble-Corrigan and Dubinin-Radushkevich isotherm models. Both the Koble-Corrigan and Dubinin-Radushkevich isotherms can predict equilibrium adsorption behaviour better at different reaction temperatures. The reaction enthalpy was 29.42 kJ/mol and the entropy achieved 164.52 J/mol·K. The change of Gibbs free energy achieved -19.48 kJ/mol at 298 K. The above indicates that the sorption process was spontaneous and endothermic. This also reveals that, fly ash has the potential for the adsorptive removal of 1,4-benzoquinone.

INTRODUCTION

As most of the organic pollutants are resistant to conventional physico-chemical and biological treatments, advanced oxidation processes (AOPs) emerge as alternative technologies for the effective removal of these organic pollutants (Andreozzi et al. 1999). AOPs are all characterized by the production of powerful and highly reactive oxygen species (ROSS) such as OH radicals (2.8 V/NHE), which present little selectivity of attack as an oxidant. A number of other oxidizing species such as H_2O_2 could be generated concurrently. Consequently, organic pollutants such as persistent organic pollutants (POPs) and endocrine disrupting chemicals (EDCs) subjected to AOPs treatment proved to be degraded effectively and even mineralized to carbon oxide, water and inorganic if the reaction time was prolonged (Peller et al. 2003, Rosenfeldt & Linden 2004, Huber et al. 2003).

However, the fundamental problem for AOPs application turns to be the high cost of the reagents such as H_2O_2 and O_3 as well as the energy consumption, such as ultraviolet irradiation in photocatalytic oxidation and electric energy in electrochemical oxidation. Due to the low degradation rates of some intermediates, it is not practical to transform all the reaction intermediates into water and carbon dioxide within a longer time frame for AOPs (Stadler et al. 2012). As a result, AOPs are always used for partial oxidation instead of complete mineralization due to their high cost (Wu & Zhou 2005). On one hand, AOPs were used for

enhancing the biodegradability of the concentrated organic wastewater before flowing to biological processes, while on the other hand, the organic pollutants in especially low concentration could be degraded to a larger extent before subjected to other operations. Totally, AOPs should be combined with other processes for the complete decontamination of organic pollutants.

Meanwhile, one unavoidable problem of AOPs has caused increasing concern as the toxicity of the degradation intermediates might become higher than their parental chemicals. For the oxidation of the aromatic pollutants, a number of organic intermediates such as catechol, quinones and organic acids have been detected in previous studies (Wu & Zhou 2005, Santos et al. 2004, Mahamuni & Pandit 2005). Other intermediates such as maleic acid and oxalic acid were detected as well. Santos and co-workers examined the toxicity of the intermediates detected in wet oxidation of phenol, and the EC_{50} values of phenol, catechol, hydroquinone and 1,4-benzoquinone are 16.7 ± 4.2 , 8.32 ± 2.7 , 0.041 and 0.1 mg/L, respectively (Mahamuni & Pandit 2005). It indicates that hydroquinone and 1,4-benzoquinone were, respectively, 3 and 2 orders of magnitude more toxic than their parent phenol. Consequently, though AOPs are powerful for the oxidation of organic pollutants, the total toxicity of the treated effluent might be higher than the raw influent.

As a by-product of coal combustion in power stations,

only a small portion of the industrial waste is utilized annually, while most of them have to be discharged into landfills. The chemical composition of fly ash is typical of the most common glassy ternary system (CaO-Al₂O₃-SiO₂) with significant amounts of transition metal oxides. It has been reported that a number of pollutants such as heavy metals and quinoline could be removed by fly ash (Rameshraj et al. 2012, Soco & Kalembkiewicz 2013, Ahmaruzzaman 2010). Utilization of low-cost fly ash for environmental decontamination is expected to be a good strategy in practical wastewater treatment. In this study, one of the oxidation intermediate generated in AOPs, 1,4-benzoquinone, was selected for the adsorptive removal by fly ash. Adsorption studies on kinetics, isotherms and thermodynamics were conducted in batch experiments to better understand the potential application of fly ash in 1,4-benzoquinone removal.

MATERIALS AND METHODS

Chemicals: Chemical 1,4-benzoquinone was purchased from the Beijing Chemical Reagent Company, and used without further purification. Other chemicals used were of analytical grade. Fly ash was obtained from Xinli thermal power plant located in Zhengzhou City (Henan province, China). Deionized (DI) water was used throughout the study.

Adsorption of 1,4-benzoquinone by fly ash: A stock 1,4-benzoquinone solution of 1000 mg/L was prepared by dissolving 1,4-benzoquinone in DI water and then the solution was treated by ultrasonic irradiation for 5 minutes. It was stored in a brown volumetric flask and kept at room temperature. The stock solution was diluted with DI water to prepare the desired 1,4-benzoquinone solutions for the subsequent batch experiments.

Adsorptive removal of 1,4-benzoquinone was determined by batch experiments in conical flasks. For kinetic study, 800 mg of fly ash was added into 1000 mL 1,4-benzoquinone solution of 10 mg/L. In the tests of adsorption isotherm and pH effect, 40 mg of the fly ash was added into 50 mL 1,4-benzoquinone solution of 10 mg/L. These mixtures were shaken at 135 rpm for 24 h to achieve equilibrium. The temperature was kept at 298 K unless otherwise stated. The solution pH adjustment was conducted by adding HCl or NaOH solution. All the solution pH values were maintained at neutral pH except for the pH effect study.

Analyses: Samples were collected and filtered through a 0.45 µm membrane before analysing. The 1,4-benzoquinone concentration of the samples was determined by measuring the maximal absorbance at a fixed wavelength (254 nm) by an UVmini-1240 spectrophotometer (Shimadzu).

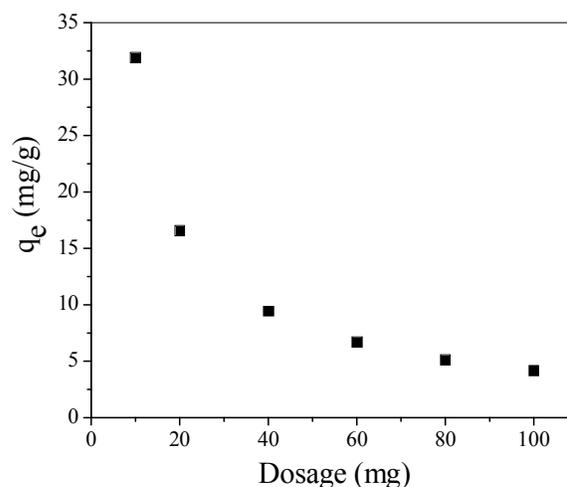


Fig. 1: Effect of fly ash dosage on 1,4-benzoquinone adsorption.

RESULTS AND DISCUSSION

Effect of fly ash dosage on 1,4-benzoquinone adsorption:

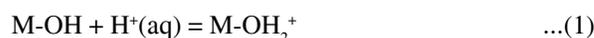
Effect of fly ash dosage was investigated for 1,4-benzoquinone adsorption, as presented in Fig. 1. The dosages of fly ash varied from 10 to 100 mg in 50 mL solution. As presented in Fig. 1, the uptake of 1,4-benzoquinone at 10, 20 and 40 mg dosage of fly ash achieved 30.9, 16.6 and 9.4 mg/g, respectively. The uptake of 1,4-benzoquinone decreased with an increase of fly ash dosage, which can be explained as following. Although the adsorption sites remained unsaturated, the adsorption sites available still increased by increasing fly ash dosage. The uptake of 1,4-benzoquinone could decline due to the increase in the vacant adsorption sites. The dosage of fly ash was selected as 40 mg in 50 mL solution in the following experiments.

Effect of solution pH on 1,4-benzoquinone adsorption:

The effect of solution pH was investigated for 1,4-benzoquinone adsorption on fly ash from pH 2.0 to 11.0, as presented in Fig. 2. It demonstrates that 1,4-benzoquinone adsorption was strongly dependent on the solution pH. Under acidic conditions, the adsorption of 1,4-benzoquinone increased gradually with an increase in solution pH from 2.0 to 7.0, while the 1,4-benzoquinone uptake decreased slightly with increasing pH from 7.0 to 11.0.

The activity of fly ash is mainly from the hydration of activated SiO₂ and activated Al₂O₃ in alkaline conditions, which could make the fly ash more positively charged in acidic conditions while more negatively charged in alkaline conditions as illustrated by the following equations:

Acidic condition:



Alkaline condition:



Though 1,4-benzoquinone molecule has low polarity, it can be deduced that 1,4-benzoquinone might be positively charged under acidic conditions, while negatively charged under alkaline conditions. As a result, the electrostatic repulsive force between fly ash particles and 1,4-benzoquinone was the lowest at neutral solution pH and consequently the highest uptake of 1,4-benzoquinone was achieved at about pH 7.0. In the following experiments, the solution pH was maintained at 7.0.

Adsorption isotherm: Adsorption of 1,4-benzoquinone at 288, 298 and 308K was simulated by Langmuir, Freundlich, Temkin, Redlich-Peterson, Koble-Corrigan and Dubinin-Radushkevich (D-R) isotherm models using non-linear regressive methods, as plotted in Fig. 3. The six isotherm models are listed below:

Langmuir isotherm (Langmuir 1916):

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad \dots(3)$$

Where C_e is the equilibrium concentration (mg/L), k_L is the equilibrium adsorption constant related to the affinity of binding sites (L/mg), q_e is the amount of 1-4-benzoquinone adsorbed onto the fly ash (mg/g), and q_{max} is the maximum adsorption capacity of the sorbent (mg/g).

Freundlich isotherm (Freundlich 1906):

$$q_e = k_F C_e^{\frac{1}{n}} \quad \dots(4)$$

Where, k_F is roughly an indicator of the adsorption capacity, and n is the heterogeneity factor, which has a lower value for more heterogeneous surfaces.

Temkin isotherm (Temkin & Pyzhev 1940):

$$q_e = A + B \ln C_e \quad \dots(5)$$

Where, A and B are the heterogeneity factors.

In the three-parameter Redlich-Peterson isotherm equation, an exponential function in the denominator has been proposed to improve the fit by the Langmuir or Freundlich equation and is given by eq. (6) (Redlich & Peterson 1959):

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad \dots(6)$$

Koble-Corrigan isotherm is a combination of Langmuir and Freundlich isotherm, as presented below (Koble & Corrigan 1952):

$$q_e = \frac{AC_e^n}{1 + BC_e^n} \quad \dots(7)$$

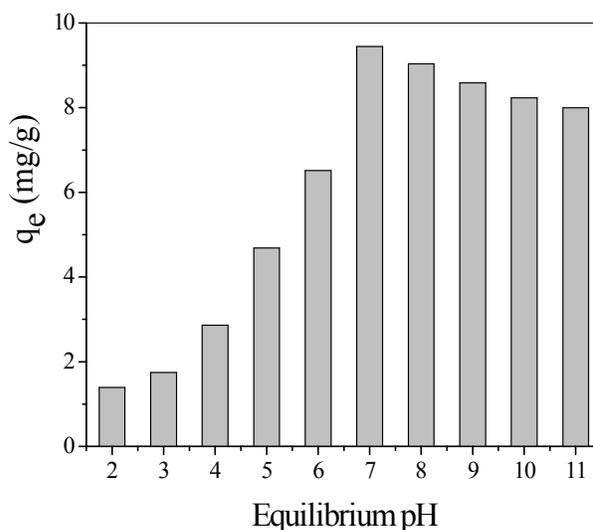


Fig. 2: Effect of solution pH on 1,4-benzoquinone adsorption.

Where, A, B and n are the Koble-Corrigan parameters.

D-R isotherm describes the adsorption on a single type of uniform pores and is given by eq. (8) (Dubinin 1960):

$$q_e = q_m e^{(-k \ln(1+1/C))} \quad \dots(8)$$

Where, k is the constant related to the adsorption energy and q_m is the maximum adsorption capacity of the sorbent (mg/g).

Fig. 3 shows the non-linear fitted curves with different adsorption models at 298 K and the relative parameters are listed in Table 1 accordingly. By comparing the experimental data and fitted curves, it was found that both the Koble-Corrigan and D-R isotherms can predict equilibrium adsorption behaviour better at different reaction temperatures. As a comparison, the values of R^2 also reveal that the Redlich-Peterson, Koble-Corrigan and D-R isotherms describe the experimental data better. Totally, Koble-Corrigan and D-R isotherm models accurately represent the experimental results, which are expected to be used for design purposes. Meanwhile, from Table 1, the determined k_F values indicate easy uptake of 1,4-benzoquinone and significant differences in sorption capacities due to different reaction temperatures. The obtained values of $1/n$ ($0.1 < 1/n < 1$) imply a higher adsorption capability for 1,4-benzoquinone at all temperatures examined. Additionally, by examining the q_m values from D-R isotherm, the adsorption of 1,4-benzoquinone increased with an increase in reaction temperatures, which indicates that the adsorption process was endothermic.

Thermodynamic parameters for the adsorption process:

Thermodynamic parameters associated with the adsorption process such as the changes in standard free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy

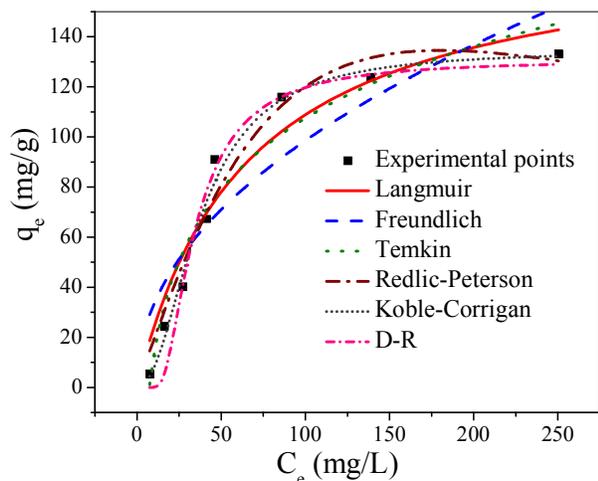


Fig. 3: Adsorption isotherm of 1,4-benzoquinone on fly ash at 298 K.

change (ΔS^0) could explain the increasing adsorption with increasing temperature. The change in free energy (ΔG^0) was estimated from the known equation (9):

$$\Delta G^0 = -RT \ln k_0 \quad \dots(9)$$

Where, the thermodynamic equilibrium constant K_0 for the adsorption process was determined by plotting $\ln q_e/C_e$ versus q_e and extrapolating to zero q_e using a graphical method (Yuan et al. 2009, Lyubchik et al. 2004). The intersection with the vertical axis gives the value of $\ln K_0$ at three different temperatures.

Values of ΔH^0 and ΔS^0 could be calculated according to the Van't Hoff equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \dots(10)$$

$$\ln k_0 = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad \dots(11)$$

In the above equations, ΔH^0 is the enthalpy of adsorption, ΔS^0 is the entropy of adsorption, R is the universal gas constant (8.314 J/(mol·K)) and T is in Kelvin. The values of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of a plot $\ln k$ versus the reciprocal of absolute temperature ($1/T$). It was found that the change in Gibbs free energy at 288, 298 and 308 K reached -18.02, -19.48 and -21.32 kJ/mol, respectively when q_e was selected as 10 mg/g. The enthalpy was 29.42 kJ/mol and the entropy achieved 164.52 J/mol·K. The above indicates that the sorption process was spontaneous and endothermic, which is consistent with the aforementioned results.

CONCLUSIONS

As one of the highly toxic intermediates during advanced oxidation processes, 1,4-benzoquinone was effectively re-

Table 1: Isotherm parameters for the adsorption of 1,4-benzoquinone on fly ash by using different non-linear isotherm models at 288, 298 and 308 K.

Isotherm model	288 K	298 K	308 K.
Langmuir			
$q_{max}/(mg \cdot g^{-1})$	157.4	180.0	227.0
$k_L/(L \cdot mg^{-1})$	0.013	0.015	0.019
R^2	0.944	0.927	0.928
Freundlich			
$k_F/(mg \cdot g^{-1})$	8.469	11.17	16.74
$1/n$	0.487	0.473	0.455
R^2	0.847	0.817	0.817
Temkin			
A	-66.78	-82.36	-75.27
B	33.34	41.23	47.65
R^2	0.923	0.936	0.904
Redlich-Peterson			
A	1.348	1.934	2.943
B	1.101×10^{-4}	3.438×10^{-4}	3.72×10^{-4}
g	1.777	1.625	1.659
R^2	0.982	0.957	0.963
Koble-Corrigan			
A	0.044	0.062	0.139
B	3.799×10^{-4}	4.631×10^{-4}	7.900×10^{-4}
n	2.068	2.118	2.057
R^2	0.995	0.983	0.976
D-R isotherm			
$q_{max}/(mg \cdot g^{-1})$	110.8	130.8	169.9
k	1191.1	893.9	670.4
R^2	0.971	0.960	0.951

moved by fly ash adsorption. Neutral and alkaline conditions were more favourable for the adsorptive removal. Kinetic analysis indicated that pseudo-first-order, pseudo-second-order and Elovich models could describe the adsorption kinetics better than the other models. Both the Koble-Corrigan and D-R isotherms can predict equilibrium adsorption behaviour better at different reaction temperatures. Thermodynamic analysis proved that the sorption process was spontaneous and endothermic.

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