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Comparison for the Adsorption of Catechol and Hydroquinone on Activated Carbon Fibre: Kinetic Analysis

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ABSTRACT

Catechol and hydroquinone are widely applied in industrial synthesis while they are typical toxic organic pollutants. Efficient adsorptive removal of catechol and hydroquinone is highly needed. In this research, activated carbon fibre (ACF) was used for the kinetic removal of the two pollutants. As catechol and hydroquinone have different pK_a values, it was found that the highest uptake of catechol and hydroquinone was observed at pH 11.0 and 5.0, respectively. The adsorption kinetics for catechol and hydroquinone were compared. The removal of hydroquinone is higher than that of catechol at almost all the pH conditions. At pH 7.0, the uptake of catechol and hydroquinone on ACF were 125.8 and 200.4 mg/g, respectively. As both Elovich and pseudo-second-order kinetic models could better describe the adsorption process, the adsorption of catechol and hydroquinone onto ACF might be chemisorption. The rate determining step might be diffusive in nature for the uptake of catechol and hydroquinone. Linear pseudo-second-order kinetic model fitted the experimental data better than pseudo-first-order kinetic model. The presence of natural organic matter, humic acid, could inhibit the uptake of catechol and hydroquinone on ACF profoundly.

INTRODUCTION

Catechol and hydroquinone are typical organic pollutants existing in natural water environment as a consequence of anthropogenic activities. Wastewater containing catechol is usually generated by several industries including rubbers, chemical, dye, photographic, pharmaceutical, cosmetics, and oil industry. This is because catechol is used as a topical antiseptic, and in photography, fur dying, leather tanning, antifungal preservation of seed potato pieces, and in polymerization inhibitors as well as a chemical intermediate, and an antioxidant in many industries (Asfour et al. 1985, Dou 1990, Schweigert et al. 2001). Nevertheless, catechol is readily absorbed from the gastrointestinal tract, causes haemolysis, degenerates the renal tubes, diminishes liver function, and accumulates in the bone marrow (Irons 1990). Meanwhile, hydroquinone is widely used in pesticides, medicine, rubber, medicine, and the fine chemicals are considered to be hazardous and toxic to some organisms and can cause vomiting, tinnitus, nausea, and abdominal pain in humans (Xue et al. 2005). Considering the acute and chronic toxicity of catechol and hydroquinone, it is highly necessary to remove them from contaminated water.

On the other hand, as undesirable and toxic intermediates, the accumulation of catechol and hydroquinone has been reported during wet catalytic oxidation and electrochemical oxidation of phenol (Santos et al. 2002, Li et al. 2014). The accumulation of cyclic intermediate organics such as catechol and hydroquinone usually occurred because the ring-opening reaction is the most difficult step during the oxidation of aromatic pollutants. Our previous study proved that activated carbon fibres (ACF) were capable of removing these cyclic intermediate organics and effectively lower the toxicity of the effluent treated by electrochemical oxidation (Li et al. 2015).

Accordingly, the adsorption process is considered to be particularly suitable for the removal of catechol and hydroquinone because of its high efficiency, low energy consumption and environment-friendliness. Thus, there is a strong desire to find a high-performance, low-cost, and easily regenerated adsorbent to remove catechol and hydroquinone from wastewater.

Some researchers consider that the excellent absorbent materials must have high specific surface area, chemical stability, and a lot of adsorption sites (Zhao et al. 2012). Meanwhile, fibrous adsorbents have advantages such as fast adsorption rate and ease of handling in comparison with granular adsorbents and powdered adsorbents. ACF have attracted wide attention due to their especially high removal efficiency and adsorption capacity. Due to its high chemical stability, ACF has been widely studied as a catalyst support for catalyst preparation or directly used as a catalyst (Adapa et al. 2006, Qu et al. 2007). As a result, it demonstrates that ACF is an ideal adsorbent to achieve high-efficiency adsorptive removal of organic contaminants. In this research, ACF was intentionally used for adsorptive removal of catechol and hydroquinone. Adsorption kinetics and solution pH effect were emphatically explored and discussed. The adsorption capability for catechol and hydroquinone was compared quantitatively.

MATERIALS AND METHODS

Chemicals: Catechol and hydroquinone (analytical grade) were purchased from Tianjin Kermal Chemical Reagents Co., Ltd (Tianjin, China) and used without further purification. The activated carbon fibre (ACF) was provided by Liaoning Anshan Senxin Activated Carbon Environmental Materials Co., Ltd (China). Its thickness is 2 mm and the average surface area is 1500 m^2/g. Deionized (DI) water was used throughout this study.

Batch adsorption studies: Stock solutions of catechol and hydroquinone (500 mg/L) were diluted to get desired concentration with DI water. Kinetic experiments were carried out in a 500 mL beaker. A desired amount of ACF (200 mg) was added to a conical flask containing 500 mL of catechol or hydroquinone solution with a concentration of 100 mg/L. The solution pH was maintained by adding 0.1 mol L^{-1} of HCl or NaOH unless otherwise stated. For the pH effect study, the solution pH was kept at neutral pH 7.0. The suspension was mixed with a magnetic stirrer at 160 rpm. Samples were collected at desired time intervals and filtered through a 0.45 μm pore-size membrane before measurement.

Analysis of catechol and hydroquinone: The concentration of catechol and hydroquinone was measured by an UVmini-1240 spectrophotometer (Shimadzu, Japan) to monitor emissions at the wavelength of 275 and 288 nm, respectively (McBrlde & Wessellnkt 1988, Yildiz et al. 2005). The adsorption capacity was calculated using the following equation:

$$q_e = (C_0 - C_e)V/W \qquad \ldots(1)$$

$$q_t = (C_0 - C_t)V/W \qquad \ldots(2)$$

Where, q_e and q_t (mg/g) are the adsorption capacity at equilibrium and time t (min); C_0 is the initial TC concentration, while C_e and C_t (mg/L) are the concentrations of TC at equilibrium and t (min), respectively; V (L) is the volume of solution, and W (g) is the mass of ACF.

RESULTS AND DISCUSSION

Effect of Solution pH on Catechol and Hydroquinone Adsorption

Solution pH can not only influence the species distribution of catechol and hydroquinone but also the surface properties of ACF. Effect of solution pH was investigated at pH 3.0, 5.0, 7.0, 9.0 and 11.0, respectively. As illustrated in Fig.1, the highest uptake of catechol and hydroquinone was observed at pH 11.0 and 5.0, respectively. It indicates that the removal of hydroquinone is higher than that of catechol at almost all the pH conditions. At pH 7.0, the uptake of catechol and hydroquinone on ACF was 125.8 and 200.4 mg/g, respectively. As there is lack of functional groups

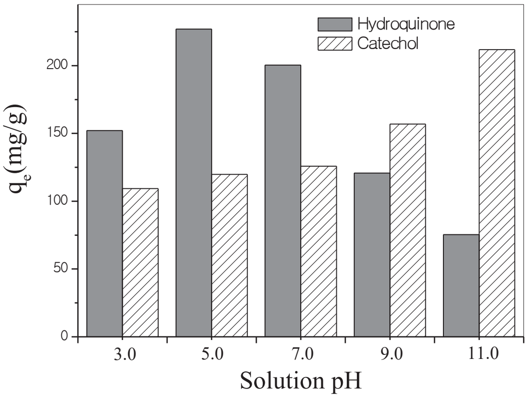

Fig.1: Effect of solution pH on the adsorption of catechol and hydroquinone onto ACF.

on ACF surface, it is deduced that the charge properties of ACF surface is quite stable. Concerning catechol (pK_a = 9.48), the catecholate anion predominates at pH ≥ 9.9, the especially higher negatively charged properties of catecholate anions might increase the electrostatic interaction and help improve the adsorption of catechol on ACF (Shakir et al. 2008). As to hydroquinone (pK_a = 10.35), the lower adsorption at higher pH may be due to the abundance of OH^- ions. The increased sorption at low pH suggests that the adsorption of the less ionic species of hydroquinone was higher than the more ionic species (Yildiz et al. 2005).

Adsorption Kinetics

As both, catechol and hydroquinone, are not stable enough for colorimetric determination in alkaline solutions, only the kinetic experiments in acidic and neutral solution were conducted for this test. The adsorption kinetics of catechol and hydroquinone onto ACF was investigated at solution pH 3.0 and 7.0, respectively. Typical kinetic models, including pseudo-first-order, pseudo-second-order and Elovich models, were used to fit the experimental data. The mathematical representations of the non-linear and linear models of pseudo-first-order and pseudo-second-order kinetics are presented below (Lagergren 1898, Ho & McKay 1999):

$$q_t = q_e(1-e^{-k_1 t}) \quad \ldots(3)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \ldots(4)$$

$$q_t = \frac{k_2 q_e^{\,2} t}{(1+k_2 q_e t)} \quad \ldots(5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \quad \ldots(6)$$

Where, q_e and q_t are the adsorption capacities (mg/g) at equilibrium and at time t (min), respectively; and k_1 (min^{-1}) and k_2 (g mg/min) are the related adsorption rate constants for pseudo-first-order and pseudo-second-order model, respectively.

The Elovich model, used to describe chemisorption occurring on the solid-liquid interface, can be written as (Kithome 1988):

$$q_t = k \ln(t) + \mathrm{a} \quad \ldots(7)$$

Where, a (g·mg/min) and b (mg/g) are constants.

Non-linear Adsorption Kinetics

The experimental kinetic data at pH 3.0 and 7.0 were fitted by three kinetic models, and the simulated curves are presented in Fig. 2. From the non-linear kinetic fitting curves presented in Fig. 2, the experimental points are much closer to the simulated curves by Elovich and pseudo-second-order kinetic models under both the pH conditions, although Elovich kinetic model seems to be the best in this case. It is deduced that Elovich and pseudo-second-order kinetic models better described the experimental points than pseudo-first-order model. At the same time, the calculated non-linear kinetic parameters are given in Table 1. The correlation coefficients (R^2) of Elovich and pseudo-second-order models are much lower than those of pseudo-second-order model. Totally, Elovich and pseudo-second-order kinetic models are more suitable to describe the kinetic adsorption process and Elovich model is the best kinetic model for the adsorption kinetics. As both Elovich and pseudo-second-order kinetic models are used to describe the chemisorption process, the adsorption of catechol and hydroquinone onto ACF might be chemisorption. Accordingly, the rate determining step might be diffusive in nature for the uptake of catechol and hydroquinone in this case (Aharoni et al. 1991).

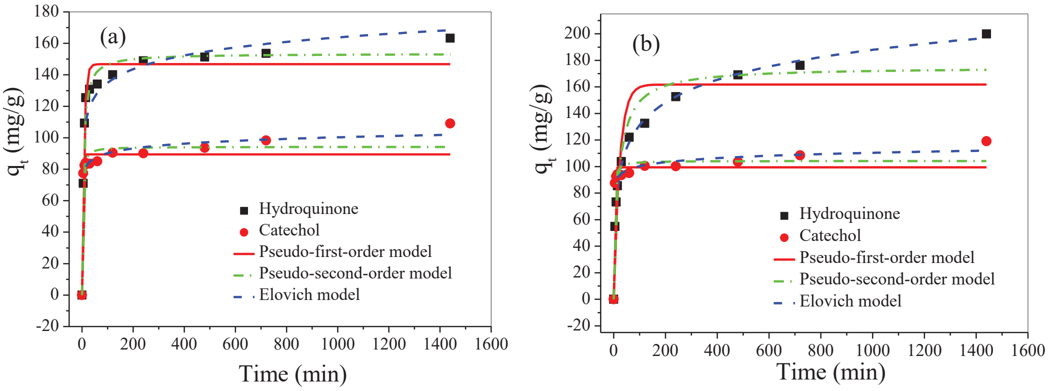

Fig. 2: Simulation of non-linear adsorption kinetics for pseudo-first-order, pseudo-second-order and Elovich models under pH 3.0 (a) and pH 7.0 (b).

Table 1: Non-linear kinetic parameters for the adsorption of catechol (CA) and hydroquinone (HQ) onto ACF.

Model	pH=3.0		pH=7.0	
	CA	HQ	CA	HQ
Pseudo-first-order model				
k_1 (min^{-1})	7.175	0.130	8.560	0.0438
q_e (mg/g)	89.38	146.8	99.49	161.8
R^2	0.895 0.902	0.964	0.914	0.860
Pseudo-second-order model				
k_2 (g/mg·min)	0.00757	0.00136	0.0078	0.00033
q_e (mg/g)	94.25	153.5	104.3	175.0
R^2	0.948 0.971	0.980	0.957	0.941
Elovich model				
a	69.75	77.01	79.86	17.28
k	4.420	12.56	4.421	24.71
R^2	0.986 0.984	0.943	0.988	0.988

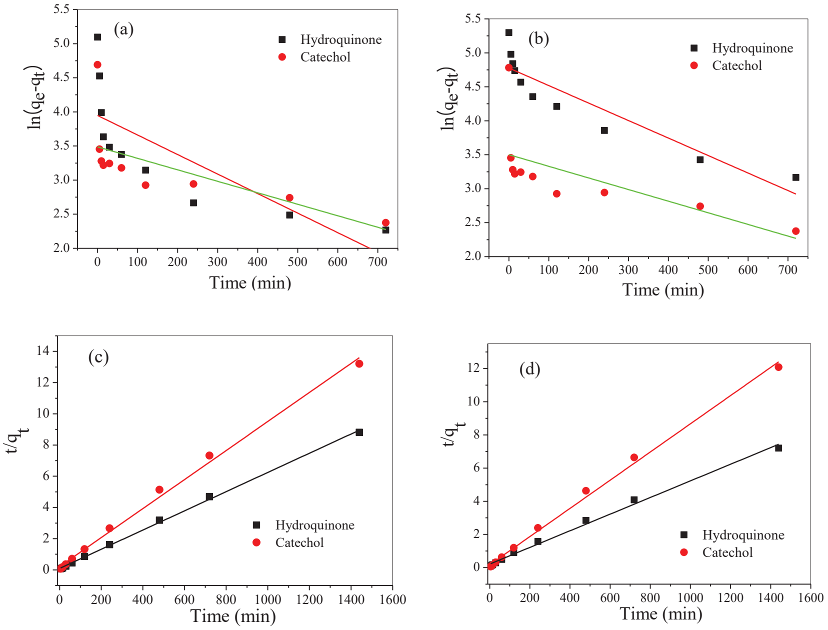

Fig. 3: Simulation of linear adsorption kinetics for pseudo-first-order (a,b) and pseudo-second-order (c,d) models under pH 3.0 (a,c) and pH 7.0 (b,d).

Linear Adsorption Kinetics

Meanwhile, both pseudo-first-order and pseudo-second-order kinetic models were employed for the linear kinetic fitting during adsorption of catechol and hydroquinone onto ACF, as illustrated in Fig. 3. By linear kinetic fitting presented in Fig. 3, pseudo-second-order kinetic model described the adsorption performance better than pseudo-first-order kinetic model. Meanwhile, the linear kinetic parameters for both models are calculated. At pH 3.0, the correlation coefficients (R^2) of pseudo-first-order models for catechol and hydroquinone are 0.569 and 0.395, respectively. As a comparison, at pH 3.0, the R^2

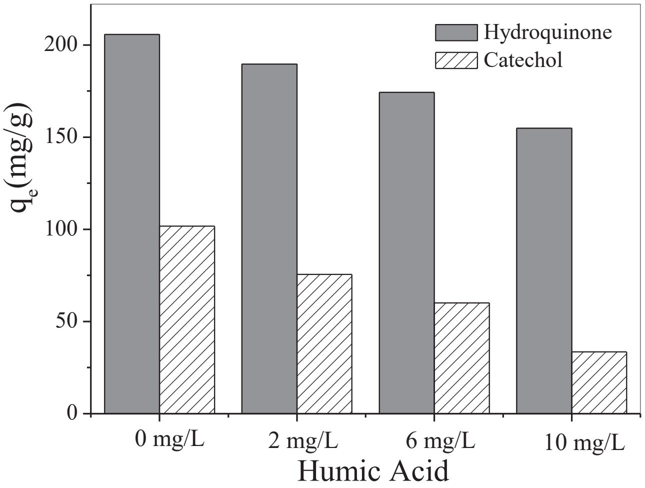

Fig.4: Effect of natural organic matter on the adsorption of catechol and hydroquinone on ACF.

values of pseudo-second-order models for catechol and hydroquinone are 0.995 and 0.995, respectively. Evidently, pseudo-second-order kinetic model better described the adsorption kinetic process. Overall, pseudo-second-order kinetic model fitted the experimental data better than pseudo-first-order kinetic model. As such, it can be inferred that chemisorption occurred during the uptake of catechol and hydroquinone on ACF.

Effect of natural organic matter on catechol and hydroquinone adsorption

Natural organic matter such as humic acid is ubiquitous in natural environment. Humic acid is a kind of macromolecule organic compound widely existing in natural water body. The existence of humic acid usually affects the adsorption and removal of pollutants from water. The effect of natural organic matter on the adsorption of catechol and hydroquinone on ACF was investigated. As presented in Fig. 4, the increasing humic acid concentration evidently decreased the uptake of catechol and hydroquinone on ACF. For catechol, the adsorption capacity reduced from 101.8 mg/g to 33.5 mg/g with an increase of humic acid concentration from 0 to 10 mg/L. For hydroquinone, the adsorption capacity reduced from 205.7 mg/g to 154.9 mg/g with an increase of humic acid concentration from 0 to 10 mg/L. As a result, the presence of humic acid could inhibit the uptake of catechol and hydroquinone on ACF profoundly.

CONCLUSION

As typical organic pollutants, catechol and hydroquinone were tentatively removed by activated carbon fibre (ACF). The highest uptake of catechol and hydroquinone was observed at pH 11.0 and 5.0, respectively. As both Elovich and pseudo-second-order kinetic models are used to describe the chemisorption process, the adsorption of catechol and hydroquinone onto ACF might be chemisorption. Accordingly, the rate determining step might be diffusive in nature for the uptake of catechol and hydroquinone. Pseudo-second-order kinetic model fitted the experimental data better than pseudo-first-order kinetic model. As such, it can be inferred that chemisorption occurred during the uptake of catechol and hydroquinone on ACF. The presence of humic acid could inhibit the uptake of catechol and hydroquinone on ACF profoundly.

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