



Study on Adsorptive Removal of 1,4-Benzoquinone by Agricultural Waste Sugarcane Bagasse

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ABSTRACT

As one of the major oxidation intermediates generated in advanced oxidation processes, 1,4-benzoquinone is proved to be highly toxic. Adsorptive removal of 1,4-benzoquinone by sugarcane bagasse, a low-cost agricultural waste, was systematically investigated. It was observed that most of the adsorption occurred within the initial 30 min. The results showed that Elovich kinetic model could better describe the kinetic data under all the solution pH conditions examined by non-linear regressive method. Pseudo-second-order kinetic model apparently fitted the experimental data better than pseudo-first-order kinetic model when using linear simulation method. The adsorption process was highly pH dependent, with the greatest adsorption occurring under neutral pH condition, and the highest uptake of 4.5 mg/g was achieved at pH 8.0. Ionic strength test indicated that 1,4-benzoquinone adsorption might form outer-sphere surface complexes with sugarcane bagasse. Natural organic matter (humic acid) significantly inhibited the uptake of 1,4-benzoquinone onto sugarcane bagasse. The study showed that sugarcane bagasse has a great potential application for the adsorptive removal of toxic 1,4-benzoquinone.

INTRODUCTION

Advanced oxidation processes (AOPs) which are characterized by the production of powerful and highly reactive oxygen species (ROs) such as OH radicals (2.8 V/NHE) have been widely used in wastewater treatment, especially for toxic industrial wastewater (Andreozzi et al. 1999). Considering the high operational cost of AOPs, partial oxidation of organic pollutants is often applied instead of complete mineralization. Though AOPs are capable of removing organic pollutants effectively and efficiently, a number of oxidation intermediates still retain in the effluents after partial oxidation, such as catechol, 1,4-benzoquinone and hydroquinone (Wu & Zhou 2001, Zhang et al. 2005, Santos et al. 2004, Naresh & Aniruddha 2006). Recent studies showed that they may pose threats to human health and break ecosystem balance. In some cases, the toxicity of the degradation intermediates is even higher than their parental aromatic pollutants. For example, 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 achieved 16.7 ± 4.2 , 8.32 ± 2.7 , 0.041 and 0.1 mg/L, respectively (Naresh & Aniruddha 2006). It indicated that hydroquinone and 1,4-benzoquinone were, respectively, 3 and 2 orders of magnitude more toxic than their parent phenol. These intermediates are expected to be resistant to conventional physico-chemical and biological treatments due

to their high toxicity. Hence, some low-cost downstream technologies are highly needed to remove the toxic oxidation intermediates of AOPs prior to discharge.

The concentrations of oxidation intermediates of AOPs vary according to the content of aromatic pollutants in the treated influent. Adsorption has been widely studied and applied in practical water treatment because of the high efficiency for various pollutants regardless of their concentration. Activated carbon is considered as the most efficient sorbent for the removal of organic pollutants mainly due to its high specific surface area and adsorption capability. However, the high fabrication and regeneration costs limit its application, especially in developing countries (Carriazo et al. 2007). Among the biosorbents available for organic pollutant removal, agricultural wastes are considered as the most potential sources as they are generated in a large amount annually while they have no prominent utilization. Meanwhile, these agricultural wastes usually contain a large amount of floristic fibre and functional groups such as carboxyl, hydroxyl, amidogen, which contributed to the possible biosorption process (Han et al. 2006). Hence, agricultural wastes could be utilized as low-cost sorbents. Recently, a number of studies have been conducted to investigate the feasibility of utilizing agricultural wastes as low-cost adsorbent for water treatment (Li et al. 2010, Han et al. 2010, Shan et al. 2012, Gupta & Suhas 2009, Zhang et al. 2011,

Ansone et al. 2014). The results showed that many pollutants could be efficiently removed by agricultural wastes. Meanwhile, the oxidation intermediates of AOPs such as 1,4-benzoquinone have low polarity so that the affinity between agricultural wastes and them will benefit the adsorptive removal.

Sugarcane bagasse is a residue from the production of sugar and ethanol, which has the potential to be used as an environmentally compatible biosorbent. In this research, the feasibility of using sugarcane bagasse as a sorbent to remove 1,4-benzoquinone, a typical oxidation intermediate in AOPs was investigated for the first time. The kinetic study was conducted to better understand the adsorption behavior. The influences of solution pH, ionic strength and natural organic matter were also investigated. These results could provide comprehensive insights to the utilization of agricultural waste for the adsorptive removal of toxic oxidation intermediates in AOPs.

MATERIALS AND METHODS

Materials: Sugarcane bagasse was collected from Guangxi province of China. It was first dried under sunlight and then grinded and screened with a 100 mesh sieve. The obtained fine powder was then dried in an oven at 333 K and stored in a desiccator for use. Chemical 1,4-benzoquinone (Bq) was purchased from the Beijing Chemical Reagent Company, and used without further purification. Other chemicals used were of analytical grade. Deionized (DI) water was used throughout the study.

Characterization of sugarcane bagasse: FTIR spectra (KBr pellets) of Bq, sugarcane bagasse samples before and after Bq adsorption were recorded on a Nicolet NEXUS 470 FTIR spectrophotometer from 400 to 4000 cm^{-1} .

Batch adsorption studies: A stock Bq solution of 1000 mg/L was prepared by dissolving Bq in DI water and then the solution was mixed in an ultrasonic bath for 5 minutes. Subsequently, the solution was stored in a brown volumetric flask and kept at room temperature in a dark place. The stock solution was diluted with DI water to prepare Bq solutions for the subsequent batch experiments.

For kinetic study, 800 mg of sugarcane bagasse was added into 1000 mL Bq solution with an initial Bq concentration of 5 mg/L. The mixed solution was stirred at a constant rate. The samples were collected at different time intervals. In other adsorption experiments, adsorptive removal of Bq was performed in a series of 100-mL conical flasks containing 50 mL Bq solution (5 mg/L). The dosage of sugarcane bagasse was 40 mg. These mixtures were shaken at 135 rpm for 24 h to achieve adsorption equilibrium. The temperature was kept at 298 K unless otherwise stated. The effect of ionic

strength was investigated at solution pH ranging from 3.0 to 11.0. The ionic strength of the solutions varied from 0.001 to 0.1 mol/L sodium nitrate. The solution pH adjustment was conducted by adding diluted HCl or NaOH solution. All the solution pH values were maintained at neutral pH except for the pH effect study.

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

$$q_e = \frac{(C_0 - C_e) V}{W} \quad \dots(1)$$

Where, q_e (mg/g) is the adsorption capacity at equilibrium; C_0 and C_e (mg/L) are the initial and equilibrium concentrations of Bq in solution, respectively; V (L) is the volume of solution, and W (g) is the mass of adsorbent used.

RESULTS AND DISCUSSION

Kinetics analysis for 1,4-benzoquinone (Bq) adsorption:

Kinetics experiment for Bq adsorption on sugarcane bagasse was conducted at pH 4.0, 7.0 and 10.0, respectively, and the kinetic data at pH 7.0 are plotted in Fig. 1. It can be observed that the adsorption process was a typical three-stage kinetic behavior, an initial rapid stage (30 min), a slower second stage (30-180 min) and a slowest equilibrium uptake stage (Vadivelan & Kumar 2005). The driving force in the initial stage was the largest and most of the adsorption occurred within this stage. The Bq removal efficiencies at pH 4.0, 7.0 and 10.0 achieved 57.7%, 66.0% and 95.3%, respectively. Compared to first and second stages, the third stage did not contribute significantly to the adsorption of Bq. As the adsorption could achieve equilibrium with 24 h, the adsorption duration was kept at 24 h in the following tests.

Pseudo-first-order and pseudo-second-order kinetics model were used to fit the experimental data (Lagergren 1898, Ho & McKay 1999). Both linear and non-linear regressive methods were used for comparison. The mathematical representations of the linear and non-linear models of pseudo-first-order and pseudo-second-order kinetics are given below:

$$q_t = q_e (1 - e^{-k_1 t}) \quad \dots(2)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \dots(3)$$

$$q_t = \frac{k_2 q_e^2 t}{(1 + k_2 q_e t)} \quad \dots(4)$$

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

Where, q_e and q_t are the adsorption capacities (mg/g) of sugarcane bagasse 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.

Elovich model was also used for the non-linear simulation. The Elovich model can be written as (Kithome et al. 1988):

$$q_t = a \ln(t) + b \quad \dots(6)$$

Where, a and b are constants.

The experimental kinetic data for Bq adsorption at pH 7.0 were firstly simulated by pseudo-first-order, pseudo-second-order and Elovich kinetic models using non-linear method, as illustrated in Fig. 1. Meanwhile, the parameters for the three models at pH 4.0, 7.0 and 10.0 are summarized in Table 1 for comparison. Judging from the values of coefficient (R^2), it can be observed that Elovich model fitted the kinetic data better than pseudo-first-order and pseudo-second-order kinetic models at pH 4.0 and 7.0. At 10.0, both pseudo-second-order and Elovich kinetic models fitted the kinetic curves better than pseudo-first-order model. In a word, Elovich kinetic model could describe the kinetic data at all the solution pH examined by non-linear regressive method.

The experimental kinetic data for Bq adsorption at pH 4.0, 7.0 and 10.0 were also simulated by pseudo-first-order and pseudo-second-order kinetic models using linear method, as illustrated in Fig. 2. Obviously, from the fitted curves, pseudo-second-order kinetic model better fitted the experimental data than pseudo-first-order model. The related parameters for both kinetic models are listed in Table 2. In all pH conditions, the value of coefficient (R^2) of pseudo-second-order model is higher than 0.99. Moreover, the calculated q_e values from pseudo-second-order model agreed well with the experimental data as well. It is reported that the pseudo-first-order kinetic model is generally applied at

Table 1: Values of pseudo-first-order, pseudo-second-order and Elovich kinetic parameters for Bq adsorption using non-linear regressive method.

| Models | pH=4 | pH=7 | pH=10 |
|-----------------------------|--------|--------|--------|
| Pseudo-first-order | | | |
| k_1 (min^{-1}) | 0.0466 | 0.0538 | 11.64 |
| q_e (mg/g) | 1.20 | 1.85 | 3.63 |
| R^2 | 0.771 | 0.876 | 0.919 |
| Pseudo-second-order | | | |
| k_2 (g/mg.min) | 0.0612 | 0.0378 | 0.1557 |
| q_e (mg/g) | 1.27 | 2.01 | 3.85 |
| R^2 | 0.877 | 0.959 | 0.993 |
| Elovich | | | |
| a | 0.2759 | 0.4342 | 2.897 |
| k | 0.1663 | 0.2647 | 2.169 |
| R^2 | 0.978 | 0.993 | 0.980 |

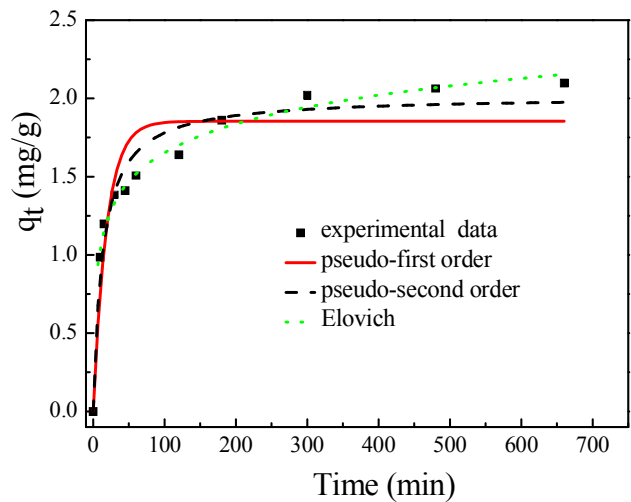


Fig.1 Pseudo-first-order, pseudo-second-order and Elovich kinetics simulation using non-linear regressive method for Bq adsorption on sugarcane bagasse at pH 7.0.

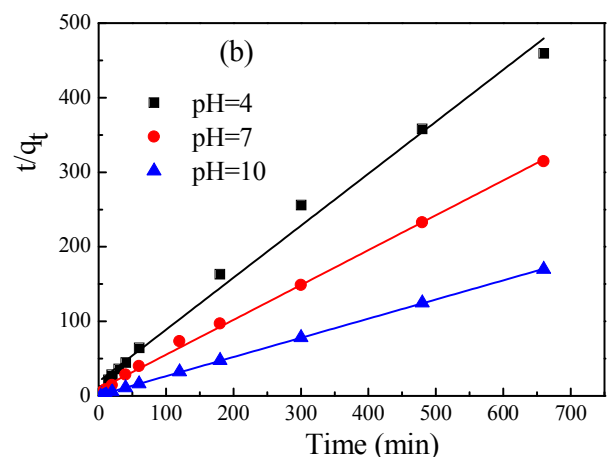
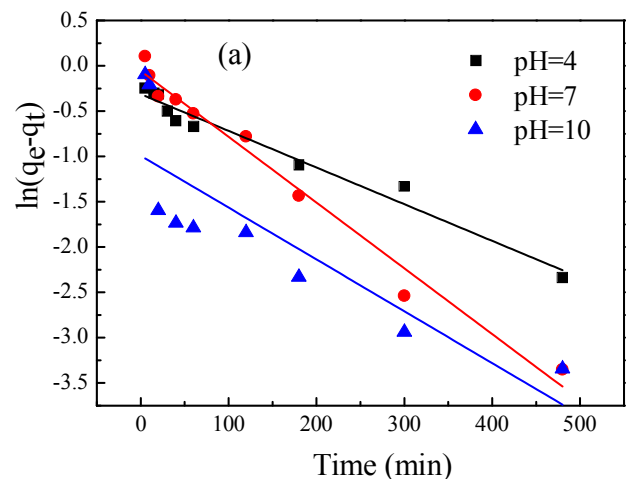


Fig.2: Pseudo-first-order and pseudo-second-order kinetics simulation using linear regressive method for Bq adsorption on sugarcane bagasse.

Table 2: Values of pseudo-first-order and pseudo-second-order parameters for Bq adsorption using linear regressive method.

| | Linear pseudo-first order model | | | Linear pseudo-second order model | | |
|-------|---------------------------------|----------------------------|-------|----------------------------------|------------------|-------|
| | q_e (mg/g) | k_f (min ⁻¹) | R^2 | q_e (mg/g) | k_2 (g/mg·min) | R^2 |
| pH=4 | 0.731 | 0.00405 | 0.968 | 1.434 | 0.02539 | 0.990 |
| pH=7 | 0.942 | 0.00725 | 0.978 | 2.139 | 0.02568 | 0.998 |
| pH=10 | 0.371 | 0.00572 | 0.685 | 3.888 | 0.08912 | 0.999 |

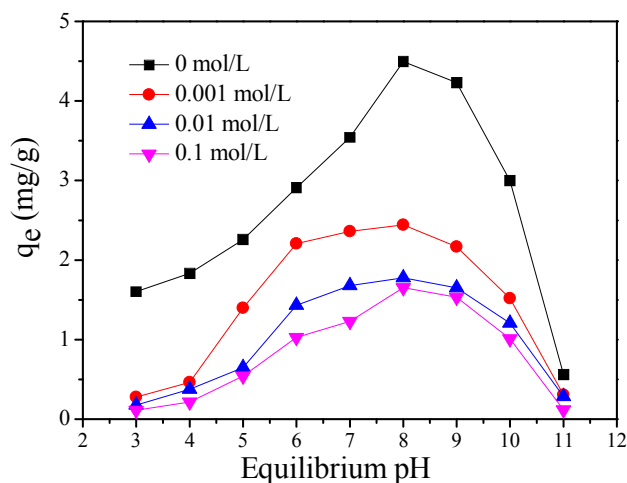
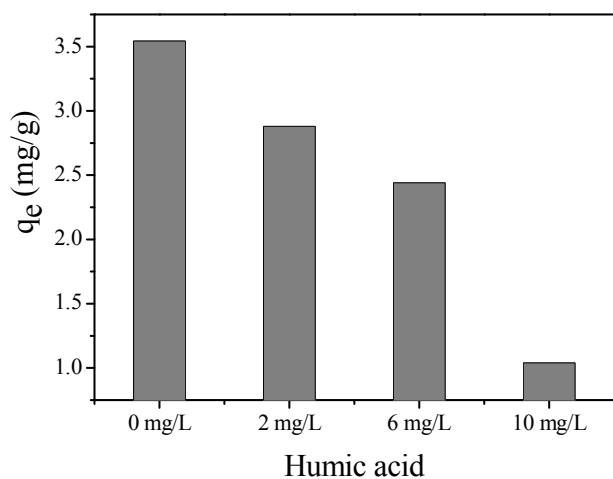
Fig. 3: Effect of solution pH and ionic strength (NaNO_3) on Bq adsorption by sugarcane bagasse.

Fig. 4: Effect of natural organic matter (humic acid) on Bq adsorption by sugarcane bagasse at neutral solution pH.

the initial stage of adsorption process while it fails to fit well to the whole range of contact time in many cases. By contrast, the pseudo-second-order kinetic model is based on the assumption that the rate-determining factor may be chemisorption and applied to the whole range of adsorption process (Wan et al. 2010). Thus, it can be deduced that the Bq adsorption process on sugarcane bagasse might be chemical adsorption.

Effect of solution pH and ionic strength on Bq adsorption:

Solution pH could affect the properties of both sugarcane bagasse and Bq molecules. Abundant functional groups such as carboxyl and hydroxyl groups are present on the surface of sugarcane bagasse. As a result, it is expected that the bagasse used is positively-charged under acidic conditions while negatively-charged under alkaline conditions. By contrast, Bq is well accepted as an electron acceptor with low polarity. The influence of solution pH on the charge properties of Bq might be insignificant. However, as shown in Fig. 3, Bq adsorption was highly dependent on solution pH, with the greatest adsorption occurring under neutral pH condition, and then decreased with increase in the solution pH. The highest adsorption capacity of 4.5 mg/g was achieved at pH 8.0. In view of the electrostatic force, it can be deduced that Bq molecules were polar enough to be positively-charged under acidic conditions while negatively-charged under alkaline conditions. Consequently, the increased electrostatic repulsion was observed with a decrease in solution pH under acidic conditions and with an increase in solution pH under alkaline conditions.

With an increase in ionic strength from 0.001 to 0.1 mol/L, Bq adsorption on sugarcane bagasse was inhibited evidently, which is presented in Fig. 3. As we know, adsorption by outer-sphere association is strongly sensitive to ionic strength. The adsorption is inhibited by competition with weakly adsorbing anions such as Cl^- and NO_3^- as a consequence of the formed outer-sphere complexes through electrostatic forces. In contrast, if the adsorption is inner-sphere association, it should show little sensitivity to ionic strength or responds to higher ionic strength with greater adsorption (Hingston et al. 1972, Al-qodah 2000). Therefore, it can be concluded that Bq adsorption may form outer-sphere surface complexes with sugarcane bagasse.

Effect of natural organic matter on Bq adsorption: Natural organic matter (NOM), represented by humic acid, is ubiquitous in surface waters. It has a high tendency to be adsorbed and might modify the properties of the sorbents involved (Giasuddin et al. 2007, Vermeer et al. 1998). The presence of NOM is expected to interfere Bq adsorption on sugarcane bagasse. The effect of humic acid on Bq adsorption was investigated and the result is depicted in Fig. 4. The

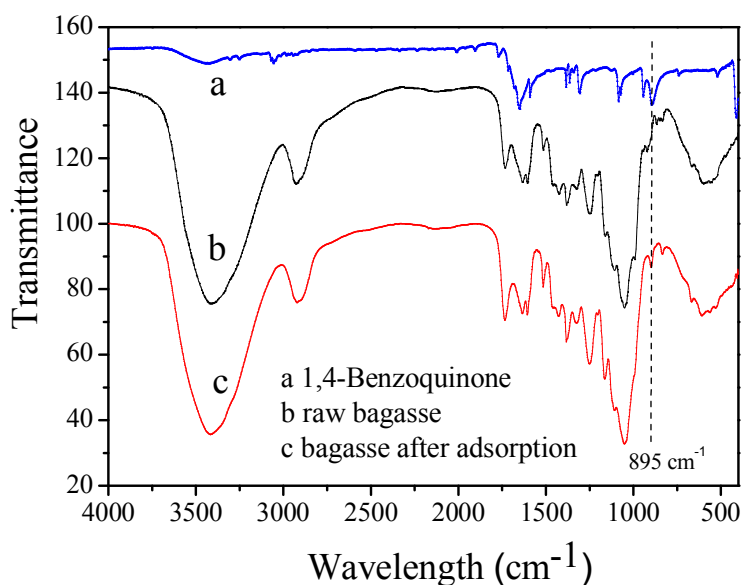


Fig. 5: FTIR spectra of 1,4-benzoquinone, raw bagasse and bagasse after 1,4-benzoquinone adsorption.

concentration of humic acid in this experiment ranged from 1 to 10 mg/L, which is close to its concentration in natural water bodies (Younger 2007). It was observed that Bq uptake decreased from 3.54 mg/g without humic acid to 1.04 mg/g in the presence of 10 mg/L of humic acid. This shows that the existence of humic acid significantly inhibited the uptake of Bq onto sugarcane bagasse.

FTIR spectra of sugarcane bagasse before and after Bq adsorption: In order to further confirm the uptake of Bq on bagasse, FTIR spectra of Bq, raw bagasse and bagasse after Bq adsorption were recorded, as presented in Fig. 5. For raw and exhausted bagasse, the absorption at 3415 cm^{-1} is attributed to the O-H stretching and that of 2920 cm^{-1} corresponds to the C-H stretching. The band at 1638 cm^{-1} is due to the bending mode of the absorbed water. The bands at 1375 and 1242 cm^{-1} originate from the O-H and C-H bending and C-C and C-O stretching, respectively. The strong band at 1048 cm^{-1} is attributed to the C-O-C pyranose ring skeletal vibration (Carvalho et al. 2011). After Bq adsorption, a new peak at 895 cm^{-1} was observed on the exhausted bagasse, which appeared on the Bq curve. The peak does not appear on the FTIR spectra of raw bagasse. These indicate that Bq molecules were adsorbed onto the bagasse.

CONCLUSION

Sugarcane bagasse was utilized as a sorbent for the efficient removal of 1,4-benzoquinone, one of the toxic oxidation intermediates in AOPs. Elovich kinetic model better described the kinetic data under all the solution pH conditions examined by non-linear regressive method. Pseudo-second-

order kinetic model fitted the experimental data better than pseudo-first-order kinetic model when using linear simulation method. Presence of humic acid significantly inhibited the uptake of Bq onto sugarcane bagasse.

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