Tetrabromobisphenol A adsorption by active carbon: influential factors and kinetics

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Abstract. Frequency detection and environmental risk of Tetrabromobisphenol A （TBBPA）in aqueous system attracted many concerns. Nevertheless, mutual interactions between TBBPA and natural or synthetic chemical materials has not be clearly revealed. In this study, influential factors, adsorption behavior and mutual dynamism of active carbon (AC) and TBBPA were comprehensively explored. It was found that chemical sorption efficiency of AC reached more than 90%. The adsorption behavior can be depicted by Langmuir and Freundlich isotherms, whose kinetic could be well described by pseudo-first-order kinetic model. The chemisorption of AC is mainly single molecular layer mode for TBBPA adsorption, during which presence of SO_4^{2-}, HCO_3^- and humic acid significantly inhibited TBBPA sorption capability. Proper temperature and pH promoted the adsorption efficiency of TBBPA. The obtained results demonstrated that AC adsorption is one feasible and effective technique for enhanced treatment technique for TBBPA containing wastewater.

Keyword. Tetrabromobisphenol A (TBBPA); Active carbon; Adsorption

1 Introduction

Recently, considerable attention has been paid to Tetrabromobisphenol A (TBBPA, $C_{15}H_{12}Br_4O_2$, CAS Registration No.79-94-7), as its occurrence and transportation in water environment. TBBPA is one typical brominated flame retardants (BFRs) that has been widely used in the manufacture of printed circuit board (PCB), due to its advantages, eg. less additive dosage, good flame retardancy and thermal stability[1]. However, TBBPA has the properties of bioaccumulation and toxicity, result to potential threat to human and animal health [2]. Thus, an effective treatment method for TBBPA removal in water is highly expected. Common techniques for TBBPA removal include photocatalytic degradation,

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adsorption, biodegradation and chemical oxidation, ect. [3-8]. However, after the wastewater containing TBBPA was treated by the wastewater treatment system, there are still many residues with rather low concentration (generally less than 10 ng L^{-1}), which could not be effectively removed by traditional biological method and advanced oxidation process.

Activated carbon (AC) is a commonly used adsorbent in adsorption technology, because of its large number of micropores and specific surface area, and there with high physical adsorption capacity. Application of AC in wastewater treatment has been characterized as high treatment efficiency and stable effluent quality, especially for the organic pollutants that are difficult to be removed by biological and chemical methods[9]. In this work, adsorption behavior of TBBPA by AC was explored and the effect of initial concentration, dosage of AC, system temperature, pH value, coexisting substances were also examined. The results may insight that adsorption of TBBPA by AC is a feasible and effective technique and give technical support for the removal of typical BFRs in the existing wastewater treatment facilities and their upgrading.

2 Materials and Methods

2.1 Adsorbent

The basic parameters of the AC coconut shell used in the experiment were shown in Table 1. The AC was firstly washed thoroughly with distilled water, and then soaked in deionized water for 24 h and dried in the oven for adsorption tests.

Table1. The parameter of AC

Parameter	Particle size (mesh)	Density （g cm^{-3}）	Intensity （%）	Iodineadsorption （mg g^{-1}）	Ash content （%）	pH
numerical value	10~28	0.45~0.54	97	1050	3	5~9

2.2 Adsorption experiments

The batch adsorption experiments were carried out in erlenmeyer flask (250 mL) that contained suitable quantity of AC, and 100 mL TBBPA stock solutions under varied environmental condition. Series of flasks were sealed and placed in a thermostatic oscillator for stable adsorption. Varied TBBPA concentration, dosage of AC, initial pH value, temperature and the concentration of co-existing substance were kept for different adsorption tests. In kinetics experiments, 2 mL solution was sampled regularly 0, 0.5, 1, 2, 4, 8, 12, 24 h, respectively, until the adsorption equilibrium reached. After centrifugal 15 min with 8 000 r min^{-1}, the concentration of TBBPA in the supernatant was analyzed by Ultra Performance Liquid Chromatography, UPLC (Waters H-Class, USA). The adsorption amounts and removal efficiency could be calculated by Eq. 1 and 2.

$$Q_t = \frac{(C_0 - C_t)V}{1000W} \tag{1}$$

$$P = \frac{C_0 - C_t}{C_O} \times 100\% \tag{2}$$

where Q_t (mg g^{-1})is the adsorption amount at time t ; C_0 and C_t in mg L^{-1} are the initial concentration and concentration at time t (mg L^{-1}); P(%) is the removal rate of TBBPA at time t ; V (mL) is the solution volume while W(g) is the total summation of sorbent.

2.3 Optimization of TBBPA adsorption by AC

The initial concentration of TBBPA, AC dosage and AC mean size, initial pH value, temperature, and the concentration of coexisting substance, were conducted to optimized the TBBPA adsorption condition parameters. The reaction temperature was 25 ± 1°C, the initial concentration of TBBPA was 1 mg L^{-1} , the dosage of AC was 0.1, 0.2, 0.5, 1.0 and 1.5 g, respectively. The removal effect of TBBPA with different amount of active carbon was examined.

2.4 Kinetics and isotherm experiments

In this study, quasi-primary kinetic model, quasi-secondary kinetic model and Elovich kinetic model were used to fit the kinetic data of adsorption of TBBPA, so as to determine the most suitable kinetic model. Analysis of adsorption kinetics is helpful to shed light on the adsorption mechanism. The pseudo-first order kinetics model was expressed as Eq. 3.

$$\log(Q_e - Q_t) = \log Q_e - \left(\frac{K_1}{2.303}\right) \text{x } t \tag{3}$$

Where Q_e (mg g^{-1}) represents adsorption at equilibrium; Qt (mg g^{-1}) represents amount of adsorbent at time t, t (min) and k_1 (1 min^{-1}) is the rate constant.

The pseudo-second order kinetics model is defined as Eq. 4.

$$\frac{t}{Q_t} = \frac{1}{(k_2 Q_e^2)} + \frac{t}{Q_e} \tag{4}$$

where k_2 (g mg^{-1} min^{-1}) is the pseudo-second order rate constant

The Elovich model is defined as Eq. 5.

$$Q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{5}$$

Where α (mg g^{-1} min^{-1}) is the initial adsorption rate and β (mg g^{-1} min^{-1}) is the desorption constant, which is the role of AC surface functionality in the adsorption of TBBPA.

Adsorption isotherms were used to describe the distribution of adsorbent molecules between solid and liquid phases. Isotherm studies were performed at designated initial TBBPA concentrations (10、15、20、25、30、32 and 35 mg L^{-1}, respectively) at 25 ± 1°C temperatures. The dosage of AC was taking out in 1 g. The adsorption isotherm of TBBPA in AC was fitted by Langmuir and Freundlich models, according to Eq. 6 and 7, respectively.

$$\frac{1}{Qe} = \frac{1}{Qe} + \frac{1}{k_L Q_{max}} \cdot \frac{1}{c_e} \tag{6}$$

Where Q_e (mg g^{-1}) is the adsorption amount of Langmuir adsorption equilibrium；C_e (mg L^{-1}) is the representative of initial concentration of TBBPA; k_L (L mg^{-1}) is the Langmuir adsorption equilibrium constant which related to adsorption capacity, and Q_{max} is the maximum adsorption capability.

$$\log(Q_e) = \frac{1}{n}\lg(C_e) + \lg(K_L) \tag{7}$$

Where n and K_F are the empirical constants which represent the relative adsorption capacity of adsorption strength and bond energy respectively. A straight line is obtained by drawing lgQ_e to lgC_e as shown in Figure 3 (c), so as to calculate the maximum adsorption volume n and the adsorption constant K_L.

3 Results and discussion

3.1 Influential factors

Impact of temperature on the adsorption of TBBPA by AC was investigated. As shown in Fig. 1 (a), the removal effeciency of TBBPA under the four temperature as 10, 20, 30 and 40 ℃ were measured. With the increase of temperature, the higher the adsorption efficiency and the faster the removal rate of TBBPA on the AC are, indicating that the adsorption of TBBPA on the AC is more favorable at medium-high temperature. It is speculated that the adsorption process of TBBPA on AC needs heat energy at different temperatures, so the proper temperature increase is conducive to the reaction.
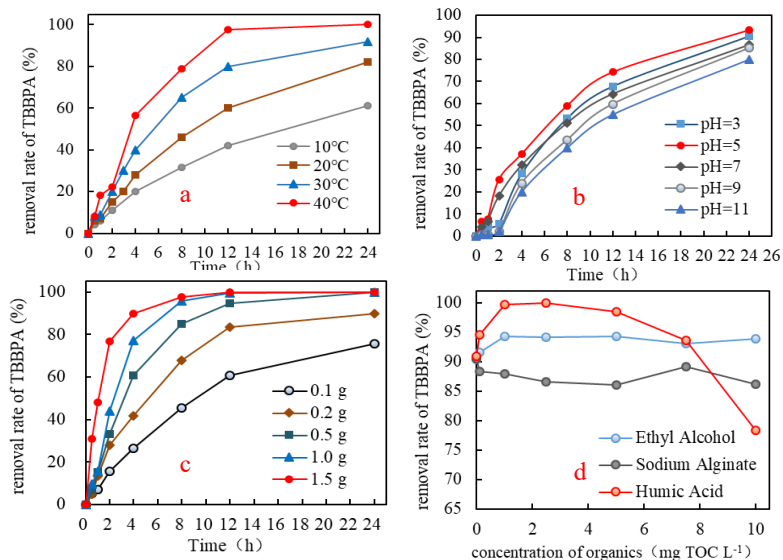

Fig. 1. The removal effect of different environment factor AC on TBBPA changes with time. (a)Temperature; (b) pH value; (c) Dosage of AC; (d) Organic dosage

Changing the pH value of the solution may lead to the change of the morphology of TBBPA and the chemical properties of the surface of the AC, thus affecting the adsorption. In the experiment, sodium hydroxide solution and hydrochloric acid are used to adjust the pH value of the solution, the pH value conditions of multiple groups of solutions are set to study the influence on the adsorption of TBBPA by the AC. The reaction is carried out under the condition of 25 ± 1℃ with an initial concentration of TBBPA of 1 mg L^{-1} and dosage of the AC of 200 mg, The test results are shown in Fig.1 (b), Acidic conditions were favorable for the adsorption and removal of TBBPA by AC. When pH=5.0, the removal rate of TBBPA by AC reached 93%.Alkaline conditions inhibited the removal of TBBPA, and the removal rate was the lowest when pH=11.0, only 80%.The reason may be related to the existing form of TBBPA, because the pKa1 and pKa2 of TBBPA are 7.5 and 8.5, respectively. When the pH value of the solution is less than 7, TBBPA mainly exists in the molecular state, so the active carbon has a very good adsorption and removal effect on it. When the pH value of the solution is greater than pKa, the ionization of TBBPA mainly exists in the form of anion, which increases the degree of ionization and dissolution in water and reduces the hydrophobicity of TBBPA, thus reducing the interaction between TBBPA and active carbon. The adsorption capacity decreased with the increase of pH value. In addition, the electrostatic repulsion between the negative charge (pH < pH_{pcz} = 8.82) on the surface of AC and the anion of TBBPA can also

reduce the adsorption capacity of AC on TBBPA.

Under the condition of initial TBBPA concentration of 1 mg L^{-1}, the effect of the amount of adsorbent on AC adsorption of TBBPA was investigated. As demonstrated in Fig.1(c), the removal rate increased while reaction time was opposite to removal effeciency as the rise up of AC dosage. The adsorption efficiency of 0.5g system is 94.6% for 12h and that of 1.5 g system is no significant improvement but reduce reaction time in 4h as the dosage changed from 0.5 to 1.5 mg L^{-1}. The increase in the amount of adsorption is mainly due to increased adsorption point and enlarged surface area due to increase dosage of AC [10]. That make magnify the opportunity of AC come into contact with TBBPA, the reaction will be accelerated and AC quickly and massively absorb TBBPA in solution. The removal rate is relatively stable with the carbon dosage further increased. This may be Limited concentration of AC result in overlapping effective adsorption points [11]. Therefore, in practical application, we should choose the appropriate dosage of AC according to the actual situation.

The co-existing organics in wastewater may affect the adsorption process of TBBPA by AC. Based on the investigation of wastewater quality, the adsorption capacity of TBBPA by AC under the influence of three coexistent organic compounds (ethanol, sodium alginate and humic acid) for 24 hours was compared and the influence of the dosage of co-existent substances on adsorption capacity by AC was explored. As shown in Fig. 1 (d), ethanol has almost no effect in the removal of TBBPA and the removal rate is kept at about 92%. The reason is that ethanol is easily soluble in water, which does not block the pore diameter of the AC and does not affect the adsorption rate of TBBPA on the AC. Sodium alginate can inhibit the removal of TBBPA. after adding sodium alginate, the removal rate of sodium alginate by AC is reduced by 5%, which may be due to the strong hydrophilicity of sodium alginate, which dissolves in water to form a thick and uniform solution, adheres to the surface of AC, occupies a part of adsorption sites, resulting in pore blockage, thus reducing the adsorption performance of AC on TBBPA. The removal rate of TBBPA in aqueous solution will be promoted by the appropriate amount of humic acid (0 - 2.5 mg TOC L^{-1}). The removal rate of TBBPA will decrease with the increase of humic acid (3 - 10 mg TOC L^{-1}). When the amount of humic acid is 10 mg TOC L^{-1}, the removal rate of TBBPA will decrease by 13%. Humic acid is a kind of macromolecular substance, and its molecular weight (10^2-10^4 dal) is large, which makes it difficult to enter into the pore diameter of AC. The adsorption capacity of AC is limited, and the adsorption of TBBPA by AC is not affected when the concentration is small. Increasing the concentration of humic acid will inevitably cause some micropores to be blocked, which will reduce the adsorption effect of AC on TBBPA. At the same time, the oxygen-containing functional groups on the surface of humic acid may produce repulsive force on the adsorption of TBBPA[12].

3.2 The effect of inorganic ions

The common cations (NH$_4^+$、Cu^{2+}) and anions (SO$_4^{2-}$、HCO$_3^-$) in wastewater may affect the adsorption of TBBPA on AC. This part of the experiment is based on the investigation of the actual wastewater quality. Under the same conditions, the initial concentration of TBBPA is 1 mg L^{-1}, the dosage of AC is 200 mg, and the reaction temperature is 25 ± 1°C. It can be seen from Fig. 2 (a) and (b) that the presence or absence of NH$_4^+$ and Cu^{2+} in the adsorption system and the concentration change have little effect on the adsorption of TBBPA by AC. Cations do not compete with TBBPA in adsorption on AC. When the dosage of SO$_4^{2-}$ exceeds 0.5 mg L^{-1}, it can promote the removal of TBBPA in Figure 2 (c). When SO$_4^{2-}$ was not added, the removal rate of TBBPA was 95%; when SO$_4^{2-}$ was added at 1.5 mg L^{-1}, the removal rate of TBBPA was increased by 4%. It can be seen from Fig.2(d) that HCO$_3^-$ has a significant effect on the removal effect of TBBPA. When the dosage of HCO$_3^-$ increased from 0 to 1.5 mg L^{-1},

removal effeciency about TBBPA decreased from 97% to 91%. While the dosage of HCO_3^- was 3 mg L^{-1}, the removal rate reached 97%, which was the same as when HCO_3^- was not added. The co-existing HCO_3^- can weaken the electrostatic attraction in the solution system, and may also compete with TBBPA for the active sites of the activated carbon, resulting in the decrease of adsorption capacity[13]. As the ionic strength increases with the increase of HCO_3^- concentration, the increase of its interaction leads to the decrease of HCO_3^- effective concentration with the decrease of activity coefficient and the decrease of the competitive ability with the active carbon of TBBPA[14].
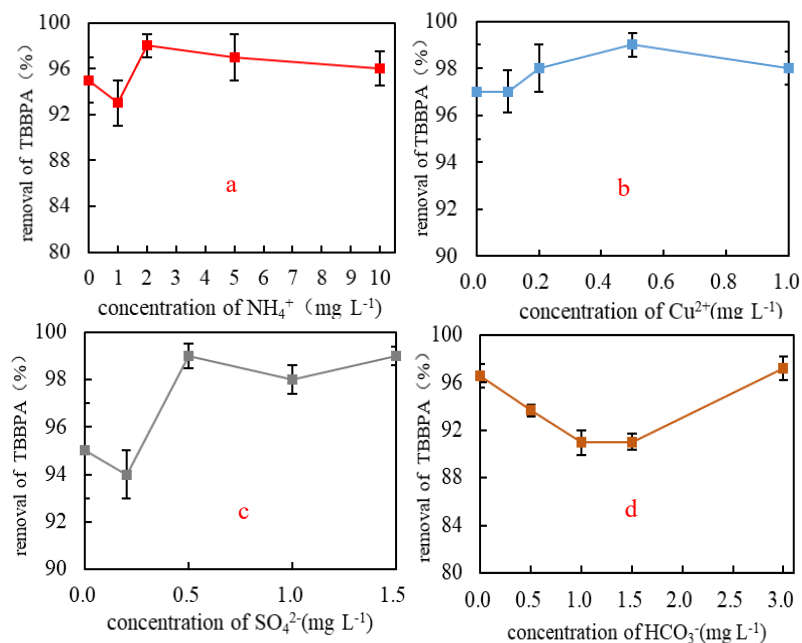

Fig. 2. Effect of inorganic ions on adsorption of TBBPA by AC, where (a) means the effect of NH_4^+; (b) means the effect of Cu^{2+}; (c) means the effect of SO_4^{2-} ;(d) means the effect of HCO_3^-.

3.3 Adsorption kinetics

The adsorption kinetic parameters can be calculated from the adsorption kinetic data, which can explain the adsorption mechanism of adsorbents in the liquid phase to some extent[15].The adsorption kinetics was analyzed using pseudo-first-order(Fig.3(a)), pseudo-second-order (Fig.3(b)) and Elovich models(Fig.3(c)). The rate limiting step of pseudo first order kinetics is determined by the diffusion of particles, while the rate limiting step of pseudo second order kinetics is determined by the number of active sites.
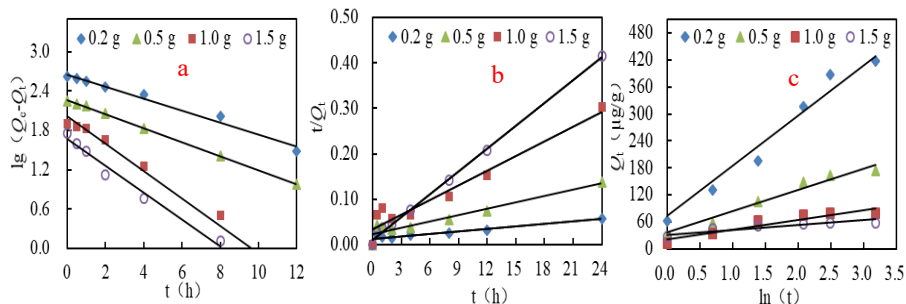
Fig. 3. Quasi-primary, quasi-secondary and Elovich kinetic models of TBBPA adsorption by activated carbon. (a) represent Quasi-primary kinetic models; (b) Quasi- secondary kinetic models ; (c) Elovich kinetic models

Table 2 lists the kinetic parameters of TBBPA adsorption on AC calculated by equation (3), (4) and (5) . The linear correlation coefficient R^2 of quasi-first-order kinetic equation is larger than that of quasi-second-order and Elovich order, so that compared with the pseudo-first order model, this model the model can reflect the adsorption mechanism of TBBPA on AC more comprehensively. In addition, it can be seen from Table 2 that with the increase of the dosage of AC, the adsorption rate constant tends to increase, that is to say, the larger the dosage of AC is, the faster the adsorption rate of TBBPA reaches equilibrium. This also indicates that chemisorption plays an important role in activated carbon, which is due to the effective electron transfer and adsorption between the active sites on the surface of TBBPA and AC.

Table 2. Kinetic parameters of TBBPA adsorption on AC

Adsorbent Quantity	Pseudo-first-order		Pseudo-second-order		Elovich model		
	K_1	R^2	K_2	R^2	R^2	α	β
0.2	0.0035	0.9822	0.0050	0.8609	0.9739	0.0036	0.1483
0.5	0.0041	0.9993	0.0167	0.9114	0.9717	0.0017	0.3517
1	0.0080	0.9864	0.0567	0.9366	0.9316	0.0010	0.7650
1.5	0.0078	0.9783	0.4150	0.9977	0.8828	0.0031	1.5350

3.4 Adsorption isotherm of TBBPA adsorbed by AC

With the rise up of equilibrium concentration, the adsorption capacity gradually increases and gradually approaches equilibrium (Fig.4 (a)), indicating that the adsorption site of AC is covered and TBBPA is more and more difficult to reach the surface adsorption site. To further explore the mechanism of adsorption, The adsorption isotherm of TBBPA in AC was fitted by Langmuir and Freundlich models(Fig.4 (b)&(c)). Adsorption isotherms can be used to describe the distribution of adsorbent molecules between solid and liquid phases. The isotherm model parameters were listed in Table 3. the adsorption of TBBPA by AC, the linear correlation coefficient (R^2) obtained by Langmuir model fitting is slightly higher than that of Freundlich model(Table 3). This shows that the energy distribution of the active site on the surface of the AC is uniform. In other words, TBBPA molecules are mainly adsorbed on the external surface of the AC in the form of a single molecular layer[16]. Once the adsorption site on the surface of AC is occupied, no further adsorption can occur at this location, which is consistent with the results in Table 3. It can also be concluded from table 4 that the maximum adsorption capacity of AC for TBBPA is 39.37 mg g^{-1}, and N = 1.1, so AC is easy to adsorb TBBPA in solution.
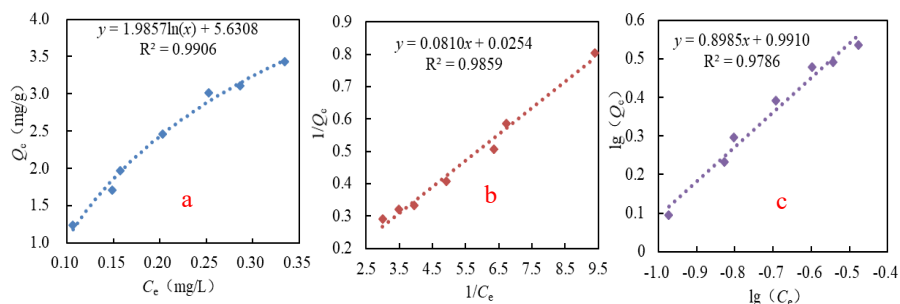
Fig. 4. Adsorption characteristics of activated carbon. (a) Isothermal adsorption curve of TBBPA by AC；(b)Langmuir isothermal adsorption model；(c)Freundlich isothermal adsorption model.

Table 3. Langmuir and lreundlich model parameters of TBBPA adsorption on AC

Langmuir			Freundlich		
R^2	Q_{max}（mg g^{-1}）	K_L（L mg^{-1}）	R^2	K_F（mg$^{1-1/n}$ L$^{1/n}$ g^{-1}）	n
0.9859	39.37	0.3136	0.9786	9.79	1.10

4 Conclusions

The removal rate of TBBPA by AC can reach more than 90%. The pseudo-first-order kinetic equation and Langmuir model can better describe the adsorption behavior of coconut shell activated carbon to TBBPA. The adsorption of AC to TBBPA is mainly monolayer adsorption, and the maximum adsorption capacity is 39.37 mg g^{-1}. The presence of SO_4^{2-}, HCO_3^- and humic acid significantly inhibited the removal of TBBPA by AC. Appropriate temperature and pH could promote the adsorption effect of TBBPA.Therefore, the removal of TBBPA from aqueous phase by coconut shell activated carbon is an effective and feasible technology.

Acknowledgements

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