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Enhanced adsorptive removal of oxidation intermediate 1,4-benzoquinone using thermally treated activated carbon fibres

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ABSTRACT

As an oxidation intermediate generated in advanced oxidation processes, 1,4-benzoquinone, a toxic intermediate has drawn increasing attentions due to its high toxicity. Activated carbon fibre (ACF) was calcined and employed for the efficient removal of 1,4-benzoquinone by adsorption. Although no noticeable change was observed on the surface morphologies of the ACF after calcination at 300℃, the results showed that the adsorptive removal efficiency of the thermally treated ACF was enhanced by 25.1% compared to the raw ACF. Energy dispersive X-ray analysis indicated that the oxygen content of the thermally treated ACF increased significantly, which might contributed to its higher adsorption capacity. Langmuir isotherm and pseudo-second-order model well fitted the experimental data. Maximal adsorption capacity of 315.2 mg/g was achieved at neutral pH and 25℃. Both neutral and acidic conditions were favorable for the 1,4-benzoquinone adsorption on the calcined ACF. The ionic strength effect experiment showed that 1,4-benzoquinone formed inner-sphere surface complexes and coexisting anions had a minor influence on the adsorption. The enthalpy and entropy of adsorption were found to be −43.62 kJ mol^{-1} and −102.51 J mol^{-1} k^{-1}, respectively, which indicates the adsorption process, was exothermic. Easy regeneration and repeated use suggest that the thermally treated ACF could be an alternative sorbent for 1,4-benzoquinone removal.

Keywords: Adsorption; Activated carbon fibre; 1,4-benzoquinone; Calcination

1. Introduction

In the last decades, advanced oxidation processes (AOPs) have received ever increasing attention for drinking water and wastewater treatment around the world. They are all characterized by the production of powerful and highly reactive OH radicals (2.8 V/NHE), which present little selectivity of attack as an oxidant. OH radicals are capable of degrading and even completely mineralizing organic pollutants into water and carbon dioxide [1]. Many AOPs including electrolysis, photocatalysis, and sonolysis have already exhibited their excellent performance on degradation of various pollutants such as phenol, persistent organic pollutants, pharmaceuticals, and endocrine disrupting chemicals [2–4].

However, most of the aromatic pollutants are not requested to be oxidized into water and carbon dioxide,

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as AOPs are used to transform organic pollutants and micropollutants into biodegradable products. Nevertheless, a number of intermediates such as catechol, quinones, and organic acids have been reported in previous studies. The accumulation of quinones usually occurred during the oxidation of aromatic pollutants because the ring-opening reaction is the most difficult step [5–7]. These changes of composition during oxidation are expected to be accompanied by an evolution of the toxicity throughout the process. For instance, Santos and co-workers examined the toxicity of the intermediates detected in wet oxidation of phenol, and concluded that 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 [8]. It indicates that the intermediates hydroquinone and 1,4-benzoquinone in the oxidation route of phenol are, respectively, 3 and 2 orders of magnitude more toxic than their parent phenol. Therefore, it is insufficient to only monitor the removal of the original pollutants and the toxicity evolution along the oxidation route should be explored from an environmental point of view. Stadler pointed out that though percent removal is always used to demonstrate the reduction of conventional pollutants in wastewater treat plants, transformation products in effluents may even exceed the parent form in both concentration and toxicity [9]. Hence, the concentration and toxicity of intermediates in the treated effluent of AOPs should be monitored and controlled before discharge, though they are powerful for the oxidation of a large variety of organic pollutants.

Since the degradation rates of some intermediates are very low, it is not practical for AOPs, from an economical point of view, to destroy all the reaction intermediates into water and carbon dioxide by prolonging the reaction time [9]. It is essential to find some downstream technologies to remove these toxic intermediates such as hydroquinone and 1,4-benzoquinone from the AOPs-treated effluents prior to flowing to next processes or discharge. Adsorption is considered one of the most effective and applicable technology for the decontamination of organic pollutants. It has been widely used for the efficient removal of a number of organic and inorganic pollutants such as phenolic compounds, surfactant, metals, and dyes [10–13]. In this study, a common oxidation intermediate in AOPs, 1,4-benzoquinone (Bq), was selected as a target pollutant subjected to the adsorptive removal. As an electron acceptor with low polarity, Bq is apt to be adsorbed onto adsorbents with low polarity. Recently, activated carbon fibres (ACFs) have drawn increasing attentions as adsorbent due to its unique properties such as high surface area, high adsorption capacity, and high adsorption rate. As a carbonaceous material, ACF has low polarity and is expected to have high affinity toward Bq, which may benefit its adsorption. In this preliminary study, the feasibility of adsorption removal of Bq by ACF was investigated. In order to increase the content of oxygenated groups on ACF and consequently improve its performance for the adsorptive removal of Bq, the ACF was tentatively treated by calcination. Besides, the adsorption kinetics and isotherm, the effect of coexisting ions on the adsorption was also studied.

2. Materials and methods

2.1. Materials and apparatus

The ACF cloth was provided by Liaoning Anshan Senxin Activated Carbon Environmental Materials Co., Ltd, China. The thickness of ACF cloth is 2 mm and the average surface area is 1,500 m^2/g. For more information about the textural and chemical properties of ACF, please refer to previous studies [14,15].

The target pollutant 1,4-benzoquinone (Bq) was purchased from Beijing Chemical Reagent Company and used without any purification. The oxidation intermediate Bq is usually prepared through electrochemical oxidation of phenol and its purity is usually comparatively low due to the coexistence of catechol and hydroquinone. Other materials used in the test were of analytical purity. Deionized (DI) water was used throughout the study.

The concentration of Bq was analyzed by UV-Visible spectroscopy (UVmini-1240, Shimadzu, Japan). The absorbance of 1,4-benzoquinone was measured at 290 nm of its maximum absorbance. The correlation coefficient of the standard curve (n = 6) was higher than 0.999. This method is also confirmed by the COD measurement. The solution pH was measured with a pH meter (Model 720A, Orion Co., USA).

The morphologies of the raw ACF and calcined ACF were recorded on a Philips Quanta-2000 scanning electron microscope (SEM) coupled with an energy dispersive X-ray (EDX) spectrometer.

2.2. Preparation of thermally treated ACF

Before used, the ACF cloth was immersed in diluted HNO_3 (0.1 M) for 24 h, washed with distilled water to remove the inorganic impurities, and dried at 80℃ in an oven. Then, the pretreated ACF cloth was calcined at different temperatures in air and used for the following adsorption tests. It should be noted that ACF could burn into ash once the calcination temperature in muffle furnace exceeded 400℃. As such, the calcination temperatures were all below 400℃.

2.3. Adsorption studies

A Bq stock solution of 500 mg/L was prepared by dissolving Bq in DI water. The stock solution was diluted with DI water to prepare Bq solution of predetermined concentration for the subsequent batch adsorption kinetics and equilibrium experiments. The equilibrium experiments were carried out in a series of conical flasks, and 50 mL of the Bq solution of 150 mg/L was used, under otherwise stated condition. A predetermined amount of the raw ACF or calcined ACF was added into the solution. The solution pH adjustment was performed using diluted 0.1 M HNO_3 or NaOH. At neutral pH condition, the mixtures were shaken on an orbit shaker at 200 rpm for 24 h at 25 ± 1˚C.

In the kinetics experiments, the samples were collected at a desired time interval and used for determination. For the coexisting ions effect experiments, different dosages of coexisting ions (SO_4^{2-}, HCO_3^{2-}, SiO_3^{2-}, F^-, and $H_2PO_4^-$) were added into the Bq solution. All the samples were filtered by 0.45 μm membrane filters before analysis.

2.4. Desorption study

The used adsorbent was collected and dried at 323 K before desorption study. First, 80 mg of the used adsorbent was transferred into 250 mL vessels containing 100 mL solution with different concentrations of NaOH (0, 0.001, 0.01, 0.1, and 0.3 M). Then, the solutions were agitated at 200 rpm for 24 h at 25 ± 1˚C. Finally, the suspensions were filtered and the concentration of Bq was analyzed. The desorbability was defined by the ratio of the desorbed Bq over the total Bq adsorbed by the adsorbent.

3. Results and discussion

3.1. Selection of calcination temperature and dwell time

In order to explore the optimal calcination temperature, Bq adsorption on the ACFs calcined at 200, 250, 300, and 350˚C was investigated. The dwell time was maintained at 1 h. The experiments were conducted in neutral pH and the result is presented in Fig. 1. It is noted that the removal efficiency increases with increasing the calcination temperature and reach the maximal at 300˚C and then slightly decreases at 350˚C. Compared to the raw ACF, the adsorptive removal efficiency of Bq is improved by 25.1% by the thermal treatment at 300˚C. It is expected that the functional groups such as –COOH, –C=O, and –OH were generated due to the calcination treatment. These functional groups have contributed to the enhanced adsorption performance. The reason why the performance of the ACF calcinated at 300˚C is better than at 350˚C might be that the very high calcination temperature could destroy these functional groups. Additionally, considering the possible burning of ACF and higher energy cost, 300˚C instead of 350˚C was selected for the following calcination treatment before adsorption test.

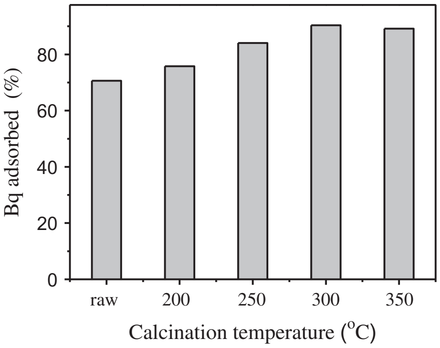


Fig. 1. Effect of calcination temperature on the adsorption removal of Bq. Calcination dwell time 1 h, initial Bq concentration 150 mg/L, sorbent dosage 800 mg/L, pH 7.0, equilibrium time 24 h.

On the other hand, the calcination dwell time is expected to affect the adsorptive removal of Bq as well. As illustrated in Fig. 2, the adsorptive removal efficiency is of 90.4, 94.2, 96.2, and 88.0% for the different dwell times of 1, 2, 4, and 6 h, respectively. This indicates that the effect of the calcination dwell time on the adsorptive removal efficiency is not ignorable. Therefore, the optimal dwell time, 4 h, was used in the following experiments.

3.2. Characterization of ACF calcined at 300˚C

Fig. 3 shows the SEM images of raw ACF and ACF calcined at 300˚C. It can be seen that there is no

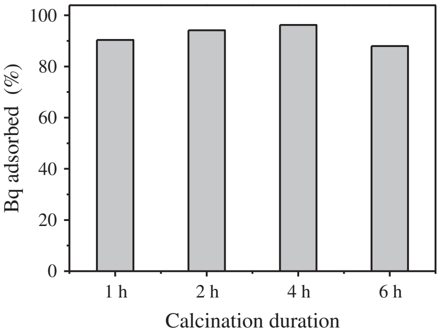


Fig. 2. Effect of calcination dwell time on the adsorption removal of Bq. Calcination temperature 300˚C, initial Bq concentration 150 mg/L, sorbent dosage 800 mg/L.

significant difference between the surface morphologies of the two adsorbents. Both the calcined and raw ACF are smooth and even. Their morphologies are similar to the observation in other studies [16]. In addition, the EDX analysis was conducted and the results are presented in Fig. 4. It can be seen that the atomic ratio of O element increased from 5.7% of the raw ACF to 10.9% of the ACF calcined at 300℃. Meanwhile, the atomic ratio of C element decreased from 93.3% of raw ACF to 88.6% of ACF calcined at 300℃. These indicate that more oxygenated functional groups such as –COOH, –C=O, and –OH might be generated due to calcination. As such, the increased amount of oxygenated functional groups on the ACF surface is expected to be capable of improving its adsorption performance.

3.3. Adsorption studies

3.3.1. Effect of the dosage of calcined ACF and kinetics study

The effect of the dosage of the calcined ACF on the adsorptive removal of Bq as a function of adsorption time was examined, as illustrated in Fig. 5. It was observed that the amount of Bq adsorbed on per gram of the calcined ACF decreased with an increase of the sorbent dosage. For instance, at 60 min, the Bq uptakes were of 237.2, 121.4, and 55.6 mg/g for the dosage of 400, 800, and 1,600 mg/L, respectively. This indicates that the adsorption sites of the ACF of higher dosage remained unsaturated during adsorption. If more Bq were added into the solution, they can be continually adsorbed on the ACF.

Additionally, it is clear that more sorbents is employed, faster the adsorption is. At the initial 30 min, the Bq adsorption is very fast and followed by a considerably longer time of slower uptake. Kinetics' data for Bq adsorption onto the calcined ACF were also studied with pseudo-first-order model and pseudo-second-order model [17–20]. The mathematical representations of the models are given in

$$q_t = q_e(1 - e^{-k_1 t}) \tag{1}$$

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

where q_e and q_t are the adsorption capacities (mg/g) of the adsorbent at equilibrium and at any time t (min), respectively; and k_1 (min^{-1}) and k_2 (g mg/min)

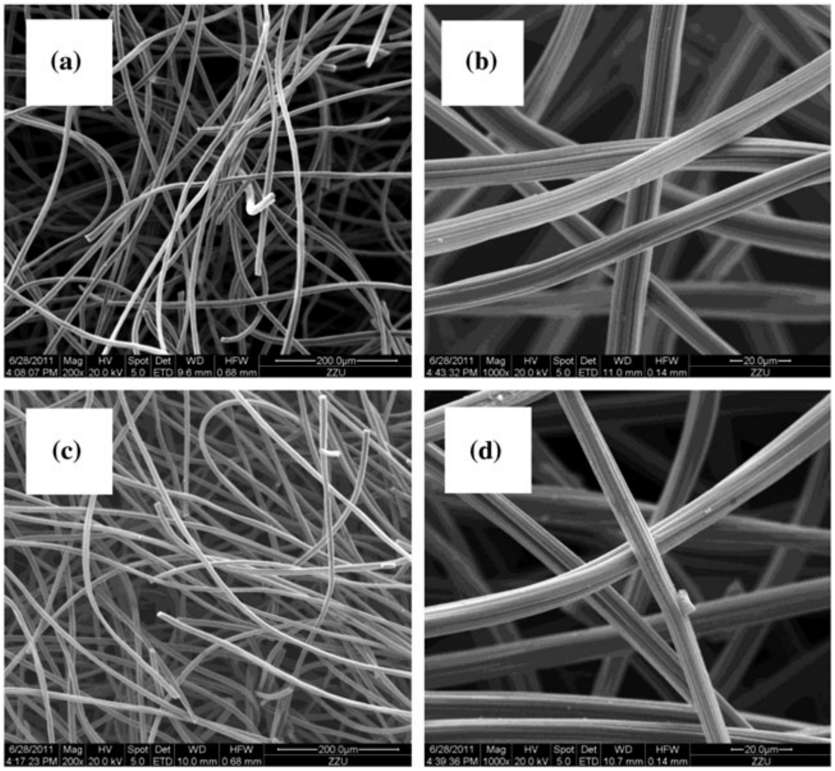
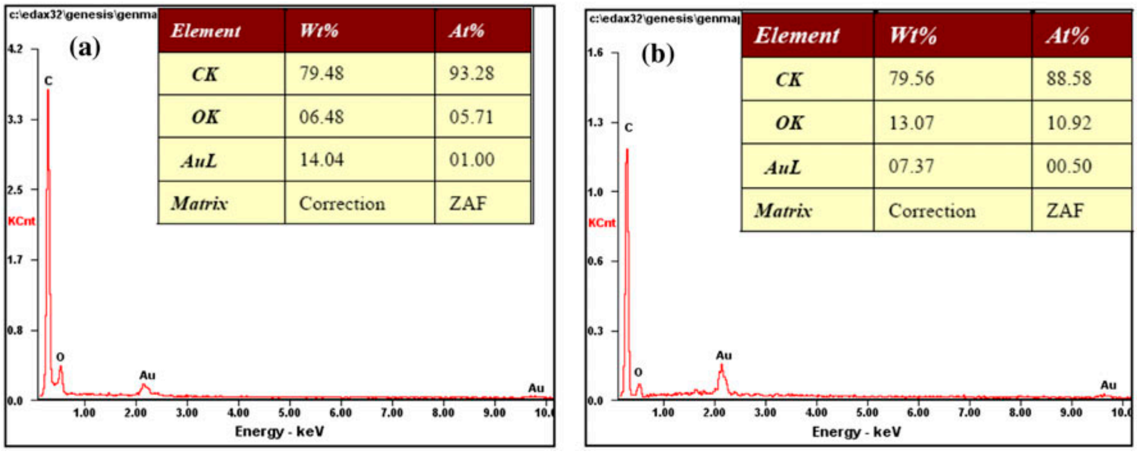


Fig. 3. SEM images of raw ACF (a, b) and ACF calcined at 300℃ (c, d).



(a)

Element	*Wt%*	*At%*
CK	79.48	93.28
OK	06.48	05.71
AuL	14.04	01.00
Matrix	Correction	ZAF

(b)

Element	*Wt%*	*At%*
CK	79.56	88.58
OK	13.07	10.92
AuL	07.37	00.50
Matrix	Correction	ZAF

Fig. 4. EDX graphs of raw ACF (a) and ACF calcined at 300˚C (b).

are the related adsorption rate constants for pseudo-first-order and pseudo-second-order model, respectively.

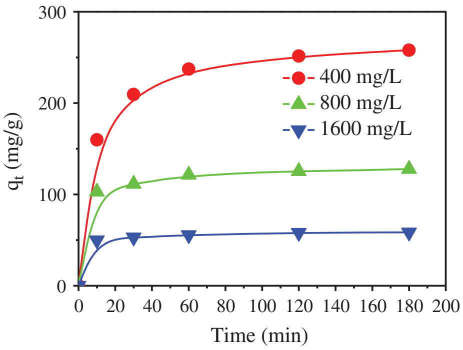


Fig. 5. Effect of the dosage of ACF calcined at 300˚C on Bq adsorption. Initial Bq concentration 150 mg/L.

The rate constants obtained from the pseudo-first-order and pseudo-second-order models are summarized in Table 1. For each dosages of the calcined ACF, the correlation coefficients show that the experimental data better fit the pseudo-second-order model than the pseudo-first-order model. In addition, the calculated q_e values from the pseudo-first-order model are not reasonable, which are even lower than the experimental q_e values. In contrast, the calculated q_e values derived from the pseudo-second-order model are very similar to the experimental q_e values. These results demonstrate that the pseudo-second-order kinetic model can better describe the adsorption process of Bq at the various sorbent dosages than the pseudo-first-order model.

3.3.2. *Effect of initial solution pH and ionic strength*

The effect of initial solution pH and ionic strength of solution on the adsorptive removal of Bq was also studied. As NaCl always exists during electrochemical oxidation, it was used as electrolyte in this investigation. As shown in Fig. 6, Bq adsorption is highly dependent on initial solution pH. The adsorption decreases with the increase in the initial solution pH. For example, in the absence of NaCl, the Bq removal efficiency decreases from 94.8% at pH 3.0 to 41.5% at pH 11.0. It has been reported that the water molecules adsorbed on ACF surface through H-bonding could block the access of Bq [21]. With the increasing pH conditions, more oxygen groups can easily be ionized and consequently more water molecules are adsorbed onto ACF surface. As such, less Bq molecules are adsorbed on the ACF and the Bq removal efficiency decreased gradually with the increasing solution pH.

The increase in ionic strength from 0.001 M to 0.1 M NaCl led to a shift in the position of the pH edge toward the alkaline region, and also enhanced the adsorption of Bq in the whole pH range from 3.0 to 11.0. Bq is well accepted as an electron acceptor with low polarity. Hence, its adsorption performance may differ from the adsorptive removal of other polar pollutants. It is well known that anions can be adsorbed via outer-sphere or inner-sphere associations. The former is strongly sensitive to ionic strength, that is, the adsorption of anions can be suppressed by the competition with weakly adsorbing anions such as Cl^- and NO_3^- since they also form outer-sphere complexes through electrostatic forces. In contrast, inner-sphere association shows little sensitivity to ionic strength or responds to higher ionic strength with greater adsorption [22,23]. Therefore, the

Table 1
Adsorption rate constants obtained from pseudo-first-order model and pseudo-second-order model for various dosages of calcined ACF

	Pseudo-first-order model			Pseudo-second-order model		
Adsorbent dosage (g)	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g mg/min)	q_e (mg/g)	R^2
0.02	42.4	223.2	0.833	5.42×10^{-4}	265.2	0.999
0.04	22.7	117.8	0.954	2.99×10^{-3}	127.1	0.996
0.08	10.9	55.0	0.975	9.44×10^{-3}	59.1	0.997

experiment results suggest that Bq may form inner-sphere surface complexes at the water/ACF interface.

3.3.3. Effect of coexisting ions

Coexisting anions such as sulfate, silicate, and carbonate are generally present in water and wastewater, which may significantly interfere in the adsorption of Bq due to competitive adsorption. In order to determine the effect of individual anion, these anions of different concentrations from 0 to 10 mM were introduced into the Bq solution before adsorption. The results are shown in Fig. 7. It was noted that sulfate, carbonate, silicate, and fluoride ions demonstrated a weak inhibiting effect on adsorption. The highest reduction in Bq removal efficiency was 15.4% which was caused by the carbonate of 10 mM. All in all, the influence of these anions is not significant even their concentrations are as high as these in natural waters [24]. However, it is worth noting that some specific wastewater containing extreme high concentration of these anions may cause a problem on adsorption of Bq by the ACF.

3.3.4. Effect of temperature on adsorption

It is known that the diffusion rate of the adsorbed molecules across the external boundary layer and the internal pores of the adsorbent particles increases, with the increasing of the adsorption temperature. This can be explained by the decrease in the viscosity of the solution. Meanwhile, changing temperature may also change the equilibrium capacity of the adsorbent for a particular adsorbate [25]. Adsorption isotherms of Bq at 25, 35, and 45℃ were obtained by varying the initial Bq concentrations. Both Langmuir and Freundlich models [26,27] were employed to describe the adsorption isotherms. The Langmuir equation is represented as:

$$q_e = \frac{q_{\max} k_L C_e}{1 + k_L C_e} \tag{3}$$

where q_e is the amount of Bq adsorbed onto calcined ACF (mg/g), C_e is the equilibrium concentration (mg/L), $q_{\max}$ is the maximum adsorption capacity of the sorbent (mg/g), and k_L is the equilibrium adsorption constant related to the affinity of binding sites (L/mg).

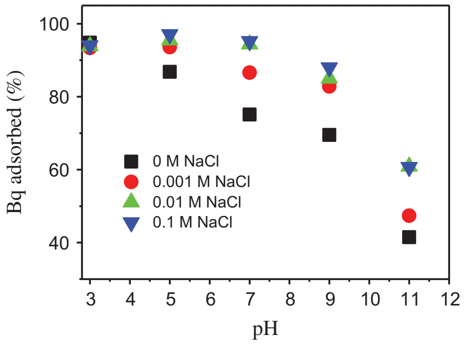


Fig. 6. Effect of initial solution pH and ionic strength on Bq adsorption on ACF calcined at 300℃. Initial Bq concentration 150 mg/L, sorbent dosage 800 mg/L.

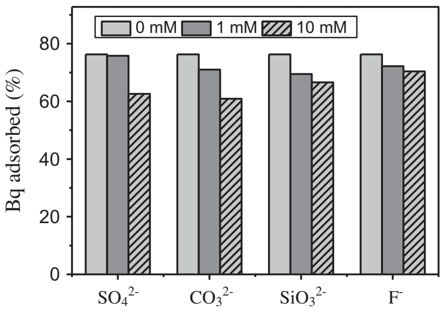


Fig. 7. Effect of coexisting anions on Bq adsorption on ACF calcined at 300℃. Initial Bq concentration 150 mg/L, sorbent dosage 800 mg/L, pH 7.0.

Freundlich model is applicable to adsorbents with heterogeneous surfaces and it can be expressed by the following equation:

$$q_e = k_F C_e^n \tag{4}$$

where k_F is roughly an indicator of the adsorption capacity, and n is the heterogeneity factor, which indicates the heterogeneous properties of a adsorbent surfaces.

The adsorption constants obtained from the two isotherms are listed in Table 2. The correlation coefficients indicate that the Langmuir model better fits the experimental data, than Freundlich model. The q_{max} values calculated from the Langmuir model is reasonable and consistent with the experimental values. Maximal adsorption capacity of 315.2 mg/g was achieved at neutral pH and room temperature. Langmuir isotherm assumes that adsorption occurs on a homogeneous surface. Conversely, the Freundlich equation describes adsorption in which the adsorbent has a heterogeneous surface and adsorption sites have different adsorption energies. Based on these results, it can be concluded that the calcined ACF might have a homogeneous surface with a monolayer adsorption of Bq.

3.3.5. Thermodynamic parameters

Thermodynamic parameters associated with the adsorption process such as standard free energy change (ΔG^{ϕ}), standard enthalpy change (ΔH^{ϕ}), and standard entropy change (ΔS^{ϕ}) were calculated using the following equations [28]:

$$\Delta G^{\phi} = -RT \ln k_0 \tag{5}$$

$$\Delta G^{\phi} = \Delta H^{\phi} - T\Delta S^{\phi} \tag{6}$$

$$\ln k_0 = -\frac{\Delta H^{\phi}}{RT} + \frac{\Delta S^{\phi}}{R} \tag{7}$$

Table 2
Langmuir and Freundlich isotherm parameters for Bq adsorption at different temperatures

	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mg/g)	k_L (L/mg)	R^2	k_F (mg/g)	n	R^2
25℃	315.2	0.1348	0.991	83.1	0.2826	0.859
35℃	288.7	0.1353	0.975	74.5	0.2838	0.866
45℃	256.1	0.0835	0.988	51.9	0.3165	0.922

where the thermodynamic equilibrium constant K_0 for the adsorption process is determined by plotting ln q_e/C_e vs. q_e and extrapolating to zero q_e using a graphical method [29]. Regression straight lines are fitted through the data points by the least-squares method. The intersection with the vertical axis gives the value of ln K_0 at the three different temperatures. In these equations, T is in Kelvin, ΔH^{ϕ} is the enthalpy of adsorption, ΔS^{ϕ} is the entropy of adsorption, and R is the universal gas constant (8.314 J mol^{-1} k^{-1}). The values of ΔH^{ϕ} and ΔS^{ϕ} can be obtained from the slope and intercept of a plot ln k versus the reciprocal of absolute temperature ($1/T$). The enthalpy and entropy of the adsorption of Bq were calculated to be −43.62 kJ mol^{-1} and −102.51 J mol^{-1} k^{-1}, respectively. The negative values of ΔG^{ϕ} −74.17, −75.20, and −76.22 kJ mol^{-1} at 298, 308, and 318 K, respectively, suggest the spontaneous nature of Bq adsorption. The negative value of enthalpy change also indicates that the adsorption process is exothermic, indicating the comparatively strong forces of attraction [30].

3.3.6. Desorption of 1,4-benzoquinone

Typically, regeneration and repeated use is one of the important capability for an adsorbent, which is directly determined by the desorption efficiency. Adsorbed Bq was separated using different concentrations of NaOH to measure the desorbability and explore the possible regeneration of the exhausted sorbent. As depicted in Fig. 8, the desorption rate of Bq increased with an increase in alkalinity from 0 to 0.3 M and the desorbability at 0.1 and 0.3 M of NaOH were of 75.7 and 77.8%, respectively. Although the adsorption of Bq is partly reversible, the Bq desorbability of 75.7% achieved by 0.1 M NaOH is satisfac-

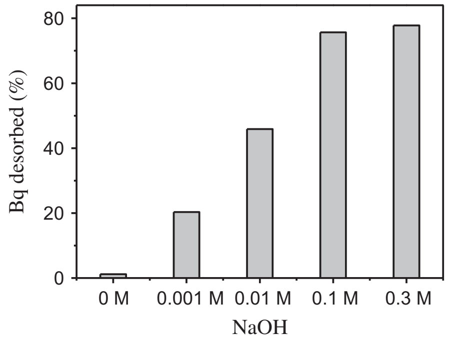


Fig. 8. Desorption of Bq using different concentrations of NaOH solution. Exhausted adsorbent dosage 800 mg/L, 100 mL solution, equilibrium time 24 h, temperature 25 ± 1℃.

tory. From this point of view, the calcined ACF has the great potential to be repeatedly used for water and wastewater treatment.

4. Conclusion

A facile method of thermal treatment was investigated to improve ACF adsorption performance in Bq removal. The results showed that the optimal calcination temperature was 300℃ in terms of the adsorption capacity. The pseudo-second-order kinetic and Langmuir model described the adsorption process very well. Maximal adsorption capacity of 315.2 mg/g was achieved at neutral pH. The ionic strength experiment indicated that the Bq may be adsorbed on the ACF via inner sphere surface complexes. Low concentration of coexisting anions did not have significant impact on Bq adsorption and thermodynamic analysis indicated that the adsorption process is exothermic. Therefore, the calcined ACF could be an alternative sorbent for Bq removal.

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