Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.24348

163 (2019) 216–223
September

Adsorption behavior of diclofenac sodium from aqueous solution using natural volcanic ash

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Received 31 August 2018; Accepted 26 April 2019

ABSTRACT

Chinese natural volcanic ash (NVA), with smooth surface and layered structure, was used for a typical pharmaceuticals and personal care products-diclofenac sodium (DCF)-removal from water. The main crystal compositions of NVA were dolomite, quartz and ankerite. To investigate the adsorption performance of NVA, batch experiments were conducted under different initial pHs (2–10), contact time (0–480 min), initial concentration of DCF (0.5–50 mg/L), temperature (298.15, 308.15, and 318.15 K), and co-existing ions (NO_3^- and SO_4^{2-}). Results showed the removal efficiency increased by 20% at optimal pH of 2 comparing to neutral solution. The kinetics evaluated in different initial DCF concentration revealed that the R^2 was higher at 5 mg/L initial DCF concentration, moreover, the data fitted pseudo-second-order model well. Results of isotherms investigated at different temperature showed that DCF adsorption on NVA was an exothermic process, and the data fitted Freudlich model very well with the value of R^2 followed 308.15 K > 298.15 K > 318.15 K. Adsorption selectivity for DCF was evaluated through analyzing the distribution coefficient (K_d). The similar K_d in the presence of NO_3^- and SO_4^{2-} (50–5,000 mg/L) showed high selectivity of NVA for DCF. This study suggested that NVA has good potential as a cost-effective adsorbent for DCF removal and its application can be expected after modification.

Keywords: Volcanic ash; Diclofenac sodium; Adsorption; Isotherms; Selectivity

1. Introduction

In recent years, pharmaceuticals and personal care products (PPCPs) have increasingly been found in various water bodies in Canada, the United States, China, Greece and other countries [1–3]. PPCPs can induce physicochemical or biochemical reaction function change and the increase of pathogenic bacteria resistance to drugs due to their high persistence, bioaccumulation and ecotoxicity even at low concentration levels [4]. In addition, because of their high polarity and solubility, complete removal is impossible in conventional water treatment plants [5]. Among the multitudinous PPCPs commonly detected in drinking water and wastewater, diclofenac (DCF), an important non-steroidal anti-inflammatory drug, is used to reduce inflammation or as analgesic, antiarthritic and antirheumatic compound [6]. It was reported that the global annual consumption of DCF is as high as 940 t [7]. Residual DCF is potentially threatening the environment and living organisms. Lonappan et al. [8] systematically summarized the toxic effects of DCF on aquatic and terrestrial organisms. It was demonstrated that DCF significantly impacts river community structure and function at even lower concentrations of 100 ng/L. Several vertebrates can be deadly affected by damaging renal and gastrointestinal tissue, and rainbow trout was a typical example. DCF may accumulate in liver kidney, gills and muscle tissues of rainbow trout and can cause cytological alterations

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1944-3994/1944-3986

even at 1 μg/L. DCF also led to the collapse of population of three Gyps vulture species (Gyps bengalensis, Gyps indicus, Gyps tenuirostris) which reduced by 98% in the Indian sub-continent, and this was included in "critically endangered" species list of International Union for Conservation of Nature [8]. Therefore, the removal of DCF from water is of great importance and imperative.

At present, many techniques such as photodegradation [9], biodegradation [10], ozonation [11], advanced oxidation processes [12] and the Fenton process [13] have been developed for PPCPs removal from water. However, these methods are usually expensive and partially efficient, and waste streams and toxic by-products may be formed during the treatment processes [14]. By contrast, adsorption method is very competitive with its advantages of high efficiency, richness and availability of raw materials, reproducibility of adsorbents, low cost and easy to handle processing equipment [15]. Different adsorbents have been used to remove DCF from wastewater. Among numerous adsorbents, activated carbon is the most common. Bhadra et al. [16] investigated the adsorption performance of oxidized activated carbon (OACs) modified from commercial activated carbon, and found that the maximum adsorption capacity of OACs on DCF adsorption was 487 mg/g. Molecularly imprinted polymer microspheres was also used to selectively remove DCF from contaminated water, and an outstanding affinity towards DCF with a binding maximum site capacity of 324.8 mg/g was achieved. It was worth mentioning that the reusability was demonstrated for at least 12 repeated cycles without significant loss in performance, indicating the promising application of adsorption in practice [14]. Comparing to commercial adsorbents, it is also valuable to explore the adsorption potential of natural materials on DCF removal.

Natural volcanic ash (NVA) is a cost-effective natural material with porous structure and strong hydrophilic surface, with the advantageous features of being very abundant and cheap in China. There are more than 660 volcanos in China, and the reserves are expected to reach tens of billions of cubic meters or more only in the Jilin Province [17]. Some researchers have used volcanic material to remove Cd (II) [18], Cr (VI) [19], and phosphate [20] from water. However, the removal of DCF using NVA has not been reported.

The present study aimed at investigating the adsorption performance of NVA on DCF removal. Some influencing factors, such as initial pH, initial DCF concentration, contact time and coexisting anions were evaluated by batch experiments. Moreover, the physical, chemical and surface characteristics, isotherms models, and kinetic models were analyzed. The mechanism of DCF removal by NVA was also discussed.

2. Materials and methods

2.1. Materials

All the chemical reagents used were of analytical grade without further purification. DCF (Dalian Meilun Biotechnology Co. Ltd., China), was dried at 105°C in an oven for 24 h and then used for the preparation of the stock solution (100 mg/L). 1 M HCl and NaOH solutions were prepared and diluted to the desired strength for pH adjustment.

The NVA used in this study was obtained from Shijiazhuang city, Hebei province, China. It was grinded and sieved until the grain size of volcanic ash was less than 150 μm, and then dried in an oven at 105°C. The dried NVA was preserved in weighing bottle to perform the adsorption experiments.

2.2. Characterization methods

Scanning electron microscope (SEM) (Nanosem 430, FEI, USA) was used to analyze the morphological features of NVA. The mineralogical phase characterization of NVA was acquired by quantitative X-ray diffraction (XRD) (D8-Focus, BrukerAXSGmbH, Germany). The functional groups present in the adsorbent before and after adsorption were analyzed by Fourier transform infrared spectroscopy (FTIR) (FTS6000, Bio-rad, USA). The surface elemental composition of NVA was studied using an energy dispersive X-ray detector (EDX) equipped on the SEM. The concentrations of DCF were measured by High performance liquid chromatography (e2695, Waters, USA). The pH of the DCF solution was determined using a pH meter (FE28, METTLER TOLEDO, China).

2.3. Batch adsorption experiments

The experiments were carried out in 50 mL test tubes. The test tubes were shaken constantly in a shaker at 150 rpm so as to ensure complete reaction at room temperature (25°C ± 1°C). Afterwards, the samples were filtered with a 0.45 μm polycarbonate filter membrane and the filtrate was used for DCF determination. The equilibrium adsorption amount of DCF was calculated as follows:

$$q_e = \frac{\left(C_0 - C_e\right)V}{M} \tag{1}$$

And the adsorption efficiency of DCF was calculated as follows:

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \tag{2}$$

where q_e is the equilibrium adsorption amount (mg/g), C_0 is the initial DCF concentration (mg/L), C_e is the equilibrium concentration (mg/L), V is the solution volume (L), M is the adsorbent mass (g) and η is the adsorption efficiency of DCF (%).

In order to evaluate the effect of pH, 50 mL DCF solution (5 mg/L) were added to the test tubes with 1 g NVA. The pH of the DCF solution was adjusted from 2.0 to 10.0, and the concentration of DCF and pH value were tested after stirring for 6 h at 25°C ± 1°C.

The isotherms study was carried out in three temperatures, 25°C ± 1°C, 35°C ± 1°C, and 45°C ± 1°C with concentrations of DCF solution varying from 0.5 to 50 mg/L (50 mL). 1 g NVA were added into the test tubes and initial pH of the solutions was adjusted to a value of 2.0.

Two concentrations of DCF (0.5 and 5 mg/L) were investigated for kinetics study. 50 mL DCF solution were added to test tubes with 1 g NVA at a contact time ranging from 0 to 480 min. After that the tubes were stirred under conditions of initial pH of 2 at 25°C ± 1°C.

The selectivity of DCF adsorption onto NVA was tested using two concentrations of DCF (0.5 and 5 mg/L) with the presence of different concentration of NO_3^- and SO_4^{2-} (a series of 50, 500, and 5,000 mg/L, initial pH 2.0, 25°C ± 1°C).

3. Results and discussion

3.1. Characterization

Table 1 shows the surface elemental analysis of NVA tested by EDX. It indicates that the main elements are carbon, oxygen, magnesium and calcium. The XRD pattern shown in Fig. 1a allows to conclude that the main crystal compositions of NVA are dolomite ($CaMg(CO_3)_2$), quartz (SiO_2) and ankerite ($Ca(Fe,Mg)(CO_3)_2$). This result was consistent with the surface elemental analysis obtained by EDX.

Fig. 1b and c show the surface morphologies of NVA before and after DCF adsorption. The SEM images showed that the NVA had a smooth surface and layered structure. Moreover, it can be seen that the surface morphology of NVA does not show obvious changes after DCF adsorption, indicating that the adsorption of low concentration of DCF would not significantly affect the surface structure of NVA.

FTIR spectroscopy can distinguish the changes of functional groups and surface properties of adsorbent. The FTIR spectra before and after adsorption of DCF onto NVA is shown in Fig. 1d. It could be seen that there were not obvious changes in the functional groups before and after the DCF adsorption, suggesting the adsorption of low concentration of DCF would not affect the functional groups of NVA. The peak at 3,620.26 cm^{-1} of the two materials was due to the vibration of (OH) group, which formed in the case that O and H can't form hydrogen bonds because of the steric hindrance or the hydrogen bond was very weak between O and H. The peaks observed at 3,019.86 and 2,895.82 cm^{-1} for the two materials are assigned to the vibration of olefin (=C–H) group and alkane (C–H) group respectively. The peak at 1,437.05 cm^{-1} of the two materials was due to the asymmetrical stretching vibration of (CO_3^{2-}) group, which is usually strong and wide, and sometimes causes two peaks. The presence of (Si–O–Si) group at 880.60 cm^{-1} was proved by the symmetrical stretching vibration.

3.2. Effect of pH

The solution pH has great effect on adsorption process. The variation of adsorption onto NVA was investigated in a wide range of pH 2~10. Fig. 2 shows that the removal efficiency was higher at low pH value, and it gradually decreased with the increase of pH. This observation was in agreement with the reports by Bhadra et al. [16] and Nam et al. [21]. The maximum adsorption capacity was obtained at pH 2 with removal efficiency of 53.8% and adsorption capacity of 0.11 mg/g under an initial DCF concentration of 5 mg/L. Fig. 2a also shows the comparison of pH change between initial pHs and equilibrium pHs. In this study, it could be easily seen that the solution pH was increased by 4.8 after adsorption when the initial solution pH was 2. It reflected the large consumption of H^+ in the adsorption process, indicating hydrogen-bond interaction may occur during the adsorption process.

Table 1
Results of the EDX analysis of NVA

	Element (wt.%)					
	C	O	Mg	Al	Si	Ca
NVA	18.46	40.84	15.21	00.72	00.23	24.54

DCF (pKa = 4.15) has neutral ion species at acidic pH (pH < pKa) and can have more affinity with NVA during the adsorption, as compared with adsorption at basic pH values (pH > pKa) [22,23]. As seen in Fig. 2b, the zeta potential of the NVA indirectly indicated that the NVA has negative surface charges in a wide range of pH values. With the increase of pH, more negative charges appeared on the NVA surface. Moreover, the DCF lost protons at pH > pKa. Then, electric repulsion occurred between dissociated (anionic) DCF and negatively charged NVA, and this phenomenon was exacerbated by the increase of pH.

3.3. Effect of temperature and isotherms

Adsorption isotherm provides theoretical maximum adsorption capacity and helps to understand the mechanism of the adsorption process or some characteristics of the adsorbent [24]. Langmuir [25] and Freundlich [26] isotherm models were used for fitting the experimental data, which are described as Eqs. (3) and (4), respectively.

$$Q_e = \frac{bQ_mC_e}{1+bC_e} \quad \text{Langmuir model} \tag{3}$$

$$Q_e = K_fC_e^{\frac{1}{n}} \quad \text{Freundlich model} \tag{4}$$

where C_e is the equilibrium concentration of DCF in the solution (mg/L), Q_e is the amount of DCF adsorbed per unit weight of adsorbent (mg/g), Q_m is the maximum adsorption capacity (mg/g), b is a Langmuir constant related to the energy of adsorption (L/mg), K_f and n are Freundlich constants related to the adsorption capacity and the intensity of adsorption respectively.

Fig. 3 shows the effect of temperature and curves of Langmuir and Freundlich isotherm models for DCF adsorption on NVA, and the parameters of isotherm models for the DCF adsorption are shown in Table 2. As Fig. 3 shows that the adsorption capacity decreased with the increase of temperature. This observation indicated that the process of DCF adsorption on NVA was an exothermic process. Similar observation was obtained with the report using Cyclamen persicum tubers based activated carbon as adsorbent [27].

As shown in Table 2, the value of correlation coefficient (R^2) of Langmuir and Freundlich isotherm models were achieved over 0.90 indicating a good mathematical by both models. The R^2 value of Freundlich model were all higher than those of Langmuir model at 298.15, 308.15, and 318.15 K, which suggested that Freundlich model was more suitable for the DCF adsorption onto NVA process. Therefore, this

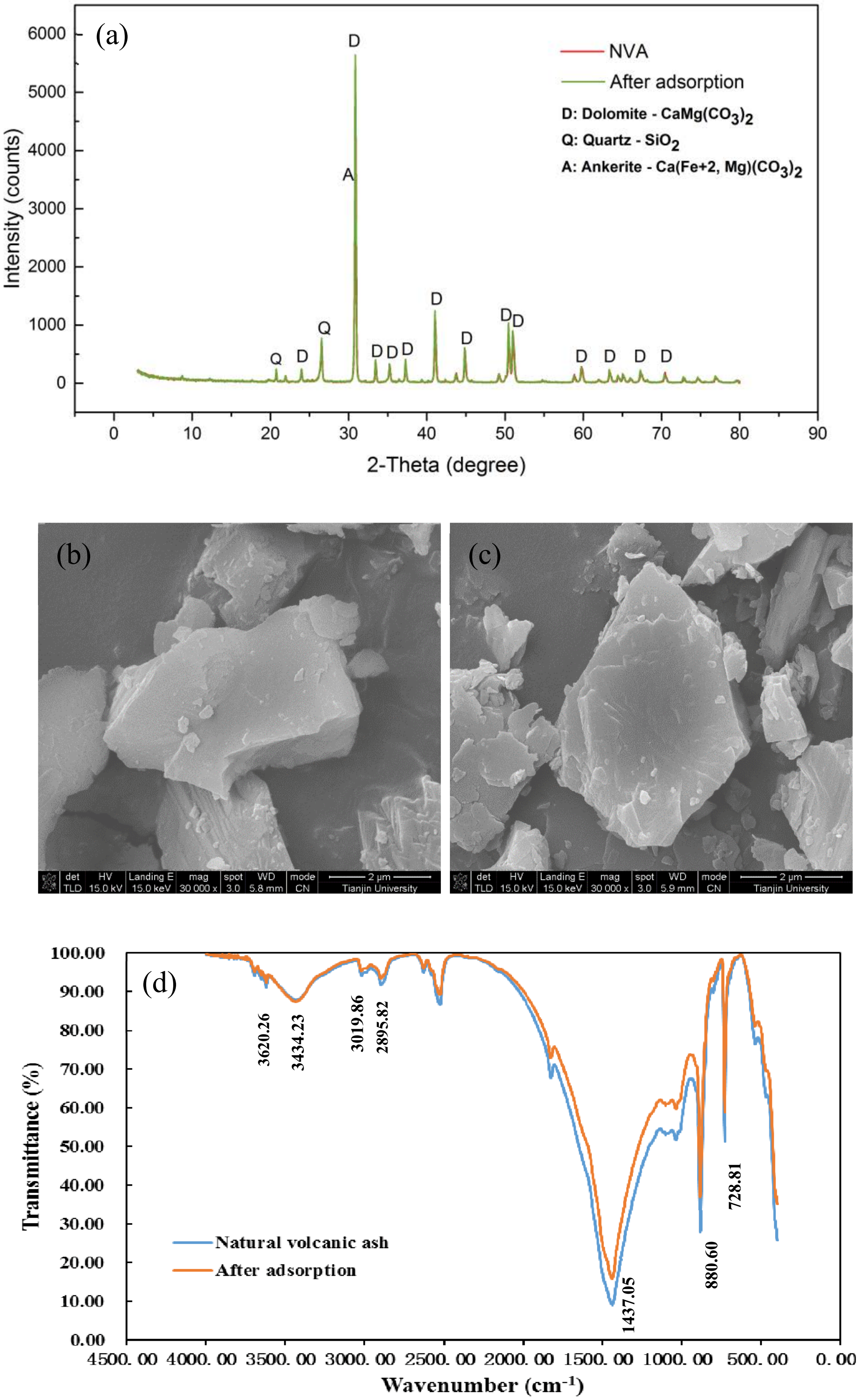

Fig. 1. XRD patterns of NVA (a), SEM images of NVA (b) and after DCF adsorption (c), and FTIR patterns of NVA (d).

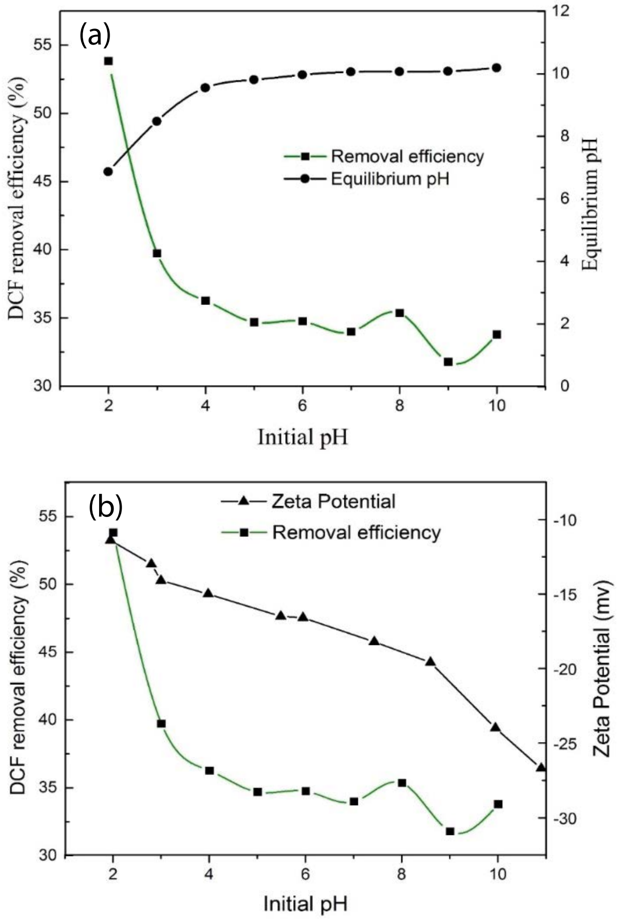

Fig. 2. Effect of pH on DCF adsorption (a) and the zeta potential of NVA and (b) (adsorbent dosage = 20 g/L, t = 360 min).

adsorption process of DCF adsorption on NVA was a complex heterogeneous adsorption process, and the surface of NVA was heterogeneous so that the surface of NVA had different functional sites with several adsorption energies [28]. The adsorbed DCF might be adsorbed on two or more adjacent adsorption sites, and the adsorbed DCF might interact with each other [29]. In addition, the constant, n, represents the adsorption intensity, and it indicates favorable adsorption when n is greater than one [30]. In this study, the n value was at around 2.5, which proved a favorable adsorption process of DCF adsorption onto NVA. The adsorption capacity of NVA was lower; therefore, the modification will be conducted in the further study.

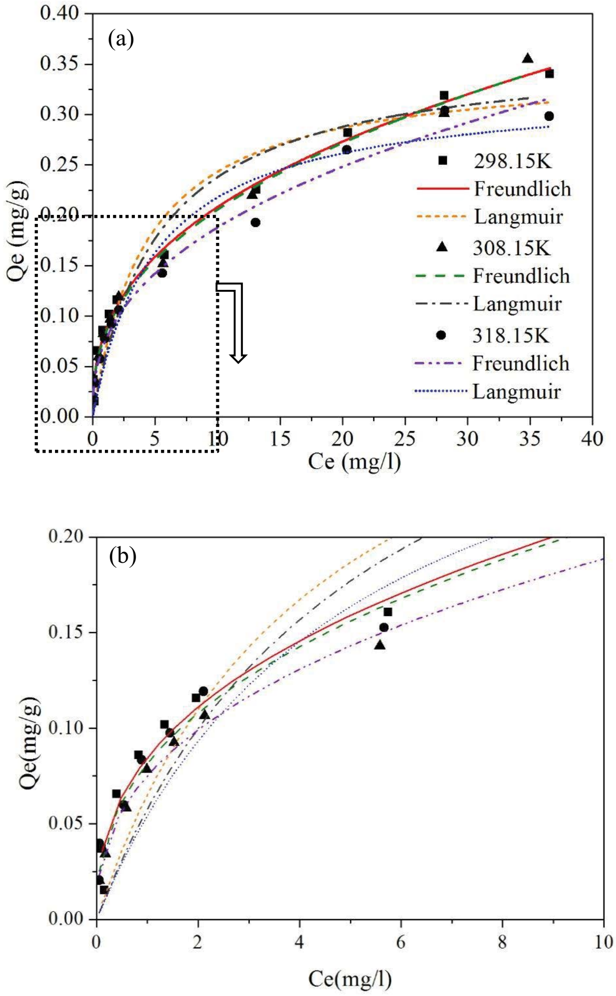

Fig. 3. Effect of temperature and curve of the Langmuir and Freundlich models for DCF adsorption on NVA (a) and magnified view of square dotted line (b). Symbols indicate experimental data (Experimental conditions: adsorbent dosage = 20 g/L, pH = 2, t = 360 min).

3.4. Effect of contact time and kinetic models

Adsorption kinetic models can reveal the potential rate-controlling step and mass transfer parameters of the adsorption process. In this study, data was fitted to two widely accepted kinetic models, namely pseudo-first-order model [31] and pseudo-second-order model [32]. And the two kinetic models are given as Eqs. (5) and (6) respectively:

Table 2
Parameters of the isotherm models for DCF adsorption on NVA

Temperature (K)	Langmuir model			Freundlich model		
	Q_m (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n	R^2
298.15	0.3490	0.2302	0.9384	0.0847	2.557	0.9913
308.15	0.3649	0.1883	0.9211	0.0817	2.489	0.9916
318.15	0.3283	0.1988	0.9403	0.0752	2.503	0.9871

Pseudo-first-order model:

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \frac{k_1}{2.303}t \tag{5}$$

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{6}$$

where t is the contact time of adsorption experiment (min); q_e (mg/g) and q_t (mg/g) are the adsorption capacity at equilibrium and at any time t respectively, k_1 is the pseudo-first-order rate constant (1/min) and k_2 is the pseudo-second-order rate constant (g/(mg min)).

The effect of contact time and kinetics on DCF adsorption is shown in Fig. 4. The adsorption process was fast at the beginning of the experiment, and as the reaction progressed, the adsorption rate became slower. The adsorption process reached equilibrium at 300 min.

Fig. 4c and d show the adsorption kinetics with initial DCF concentration was 0.5 and 5 mg/L respectively, and the corresponding parameters are summarized in Table 3. The value of $k_2q_e^2$ of pseudo-second-order model can be considered the initial adsorption rate [32]. It can be seen from Table 3 that the R^2 value of pseudo-second-order model and $k_2q_e^2$ term value were increased when the initial DCF concentration increased. The observation suggested that with the increase of the initial DCF concentration, the external mass transfer control on the adsorption process enhanced and the initial adsorption rate increased. Besides, it was obvious that the correlation coefficients of pseudo-second-order model were higher than those of pseudo-first-order model, indicating a better fit to the experimental data.

3.5. Selectivity

The anion components are always complex whether in natural water or in sewage. The presence of coexisting ions may affect the adsorption process. Therefore, the selectivity is an important factor for adsorption process and the practical application of adsorbent. The adsorption affinity of DCF was been investigated in the presence of NO_3^- and SO_4^{2-} anions, which have different molecular dimensions, charge density and hydration degree. This study was conducted with two initial DCF concentration, 0.5 and 5.0 mg/L, and the concentration of coexisting ions were set from 50 to 5,000 mg/L based on the rationale that the concentration of the coexisting ions NO_3^- and SO_4^{2-} range from hundreds to several thousand mg/L in actual wastewater [33]. The adsorption affinity is often represented in term of the distribution coefficient, K_d (mg/L), which can be calculated as [34]:

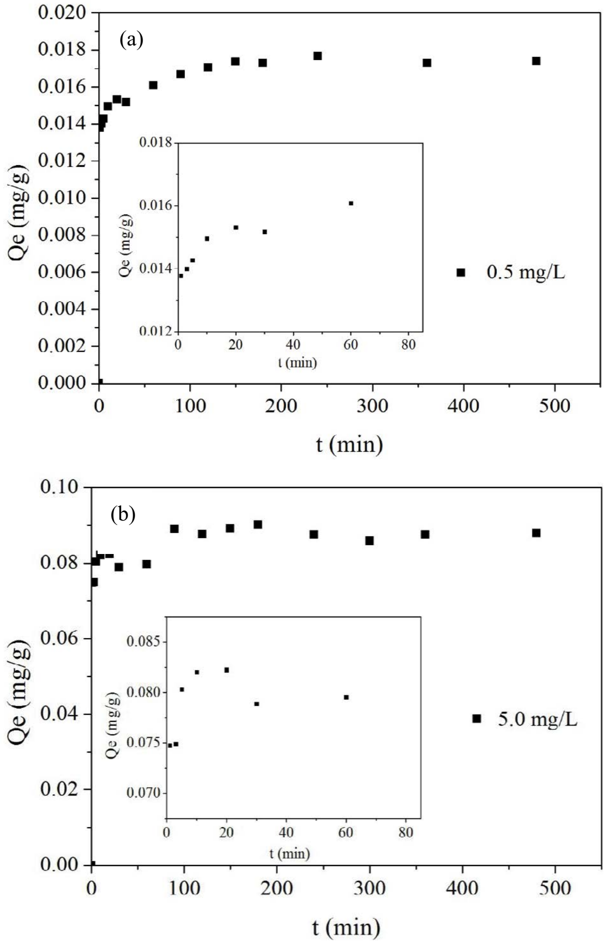

Fig. 4. Effect of contact time of DCF adsorption onto NVA (a, b), Plots of pseudo-first-order kinetic model (c), and pseudo-second-order kinetic model (d). (Experimental conditions: adsorbent dosage = 20 g/L, pH = 2, T = 25°C ± 1°C).

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{M} \tag{7}$$

where C_0 and C_e are the initial and equilibrium concentration of DCF in the solution respectively. V is the volume of solution (mL), and M is the amount of NVA (g). The distribution coefficient denotes the binding affinity of DCF to NVA. A higher K_d value indicates a stronger binding affinity. The K_d

Table 3
Parameters of the kinetic models for DCF adsorption on NVA

Initial DCF concentration (mg/L)	Pseudo-first-order model			Pseudo-second-order model		
	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	$k_2q_e^2$ (mg/(g min))	R^2
0.5	0.0029	0.0065	0.5871	0.0175	0.0089	0.9996
5.0	0.0101	0.0045	0.2805	0.0878	0.1088	0.9998

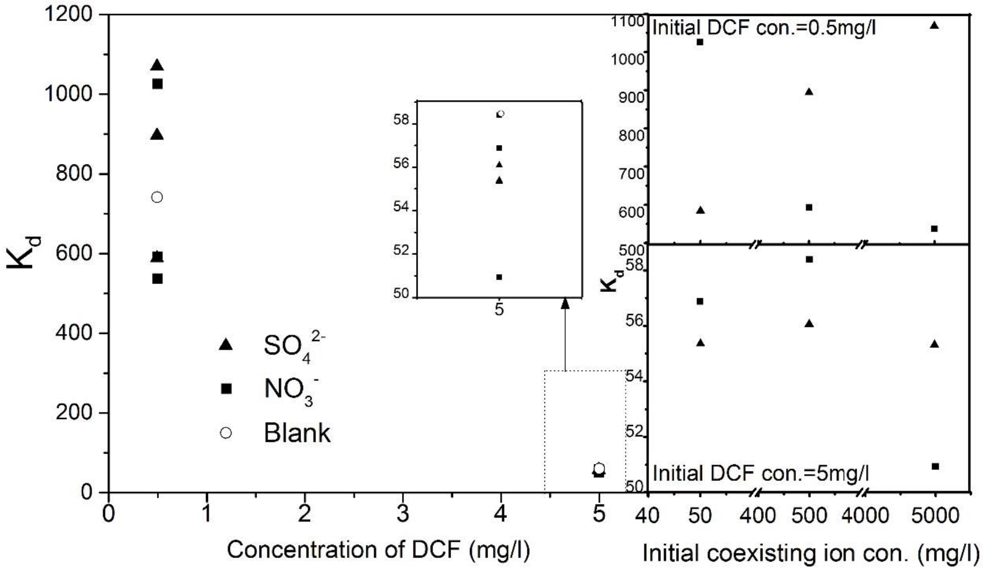

Fig. 5. Variation in the distribution of coefficients of DCF in the presence of coexisting ions. (Experimental conditions: adsorbent dosage = 20 g/L, pH = 2, T = 25°C± 1°C, t = 360 min).

values of DCF in the presence of NO_3^- and SO_4^{2-} are shown in Fig. 5.

Fig. 5 shows that the K_d value was much higher when the initial DCF concentration was 0.5 mg/L, as compared with an initial concentration of 5.0 mg/L. It indicated that the DCF and NVA have stronger binding affinity at lower DCF concentration. Moreover, the K_d value showed great variation at the initial DCF concentration of 0.5 mg/L, while it remained stable at initial DCF concentration of 5.0 mg/L. And it suggested that the concentration of coexisting ions had greater effect to adsorption affinity between DCF and NVA at lower DCF concentration. When the DCF initial concentration was 0.5 mg/L, the K_d value was decreased as the NO_3^- concentration increasing, and on the contrary, the K_d value was increased as the SO_4^{2-} concentration increasing. Moreover, the concentration of NO_3^- and SO_4^{2-} had no change based on the test results from ion chromatography. This result indicated that with the increase of concentration, the interference of SO_4^{2-} on the adsorption process becomes weaker, and the interference of NO_3^- on the adsorption process becomes stronger at low initial DCF concentration.

But in general, the K_d value changes by more than one order of magnitude imply a strong effect by coexisting ions, K_d values of the same order of magnitude change always indicate slight or no effect when coexisting ions exist. In this study, the K_d value changed within one order of magnitude implying DCF adsorption on NVA would not be affected when NO_3^- and SO_4^{2-} ions are present at high concentrations in the solution, thus indicating that the NVA has good adsorption selectivity for DCF.

4. Conclusions

In this study, the adsorption properties of Chinese NVA used for DCF removal were evaluated by batch experiments. Results showed that the optimum initial pH value of DCF adsorption on NVA was 2. The large gap between initial pHs and equilibrium pHs reflected the large consumption of H^+. The process of DCF adsorption on NVA reached equilibrium at 300 min, and they were well described by pseudo-second-order kinetic model. Moreover, this adsorption process was exothermic process, and the equilibrium data fitted Freudlich isotherm very well. NVA is of high selectivity on DCF adsorption. The results of characterization showed that the NVA had smooth surface and layered structure, and the main crystal compositions of NVA were dolomite, quartz and ankerite. The use of NVA as an adsorbent for DCF removal is potential and may provide an alternative method for DCF removal from contaminated water.

Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgement

The research was sponsored by the National Natural Science Foundation of China (Project No. 21507101, China).

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