

## Article

# Adsorption of Isothiazolone Biocides in Textile Reverse Osmosis Concentrate by Powdered Activated Carbon

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**Abstract:** Isothiazolones have been widely applied as non-oxidizing biocides to prevent biofouling of reverse osmosis (RO) membranes. However, few studies have investigated suitable RO concentrate treatments to remove these biocides. This study evaluated the adsorption behavior of four isothiazolone biocides, 2-methyl-4-isothiazolin-3-one (MIT), 5-chloro-2-methyl-4-isothiazolin-3-one (CMIT), 1,2-benzisothiazol-3(2H)-one (BIT), and 2-n-octyl-4-isothiazolin-3-one (OIT), by powdered activated carbon (PAC). Isothiazolones adsorption was found to obey pseudo second-order kinetics. Langmuir adsorption isotherms were more suitable to simulation of the adsorption effects than Freundlich isotherms. The adsorption amount followed the order OIT > BIT > CMIT > MIT, in accordance with the isothiazolones octanol/water partition coefficients ( $K_{ow}$ ), indicating that hydrophobicity is the main factor for influencing adsorption amounts. Following normalization with  $K_{ow}$ , the amounts of isothiazolones adsorbed at equilibrium and normalized aqueous concentrations showed a linear relationship in a log-linear form. 1,2-benzisothiazol-3(2H)-one is anionic at high pH, and difficult to adsorb, while neutral BIT is more likely to be adsorbed. Textile reverse osmosis concentrate had an adverse effect on MIT, CMIT and BIT adsorption, but little effect on adsorption of OIT, which has a high log  $K_{ow}$  value. There was competition between organics and isothiazolones for PAC adsorption sites, which influenced the adsorption efficiency.

**Keywords:** isothiazolone biocides; activated carbon; reverse osmosis; adsorption

## 1. Introduction

Biocides have been used in a wide array of applications to protect materials from biological erosion caused by microorganisms. Isothiazolones, which are a class of biocides that have been produced industrially since the 1970s, are widely used in cosmetics, textile applications and building products [1]. Isothiazolones are released from building products in both wet and dry weather conditions [2], after which they can enter the soil, surface or groundwater, where they hinder microbial growth [3].

Wastewater reclamation is a promising method to achieve sustainable water management, and alleviate water scarcity in the long-term [4]. High quality reclaimed water can be attained using reverse osmosis (RO) during wastewater treatment and reclamation. Suitable pre-treatment can decrease membrane fouling caused by microorganisms in wastewater that adhere to and produce extracellular polymeric substances on the membrane [5]. The non-oxidizing biocide Kathon™ (2-methyl-4-isothiazolin-3-one, MIT/5-chloro-2-methyl-4-isothiazolin-3-one CMIT: 1:3) is usually added at a concentration of  $7.5 \text{ mg}\cdot\text{L}^{-1}$  as a pre-treatment for RO systems, to maintain stable operational conditions; however, isothiazolones are retained in the RO concentrate (ROC) [6].

Isothiazolones can pass through cell membranes and fungal cell walls, after which they conduct nucleophilic attack of intracellular sulfur atoms in biomolecules such as proteins and small molecules, to impair cell functions [7]. For instance, 1,2-benzisothiazol-3(2H)-one (BIT) is highly toxic to zebrafish embryos [8], and BIT can inhibit the activity of enzymes such as phosphatases [9]. Moreover, a CMIT/MIT mixture can cause allergic reactions, and the halogenated groups induce CMIT sensitization [1]. The median lethal concentration (LC50) of MIT for *Daphnia magna* is  $18.2 \mu\text{mol}\cdot\text{L}^{-1}$ , and its primary ozonation product remains toxic [10]. Biocides that are discharged into natural water systems without appropriate treatment may cause potential environmental and toxicological problems [11]. Particularly, isothiazolones have been found to lead to high genotoxicity, and must therefore be removed from ROC [6].

Carbon materials have been widely applied as adsorbents for the removal of pollutants from potable water and/or wastewater. Recent studies have focused on the mode of dosage for PAC [12,13], and the adsorption process of different pollutants, such as oseltamivir [14] and dyes [15]. There have been many investigations of the adsorption equilibrium, adsorption kinetics, and activation energy conducted to evaluate the adsorption process. The equilibrium can be fit by Dubinin-Radushkevich (D-R) to determine the adsorption nature, while the rate constant of adsorption kinetics and temperature can be used to determine activation energy [16,17]. Powdered activated carbon has also been shown to have a higher adsorption capacity and rate constant than granular activated carbon (GAC) of pentafluorophenol [18]. For some carbon nanotubes, the adsorption affinity was poorly correlated with hydrophobicity, but increased in the order of nonpolar aliphatics < nonpolar aromatics < nitroaromatics [19]. The specific adsorption mechanisms of many compounds have been studied, especially organics, and a complex interplay between electrostatic and non-electrostatic interactions is known to occur during adsorption onto carbon materials. Electrostatic interactions usually occur when organic sorbates are ionized, while non-electrostatic interactions result from dispersion and hydrophobic interactions. [20] Theoretical and experimental studies of isothiazolinone adsorption onto ordered mesoporous silica have also been conducted, and the results showed that adsorption mainly depended on the particle size of the silica support [21]. However, no studies have been conducted to investigate the adsorption processes of isothiazolone biocides by PAC from actual ROC.

In this study, the process by which different isothiazolone biocides, including MIT, CMIT, BIT, and 2-n-octyl-4-isothiazolin-3-one (OIT), were adsorbed to PAC was investigated, and the different isothiazolones adsorption isotherms were then simulated. In addition, the influence of pH on isothiazolones adsorption was studied, and the actual textile ROC was used to estimate the impact on the amount of isothiazolone biocides adsorbed during various engineering practices.

## 2. Materials and Methods

### 2.1. Materials and Reagents

The coal-based PAC was supplied by Paleo Energy Technology CO., LTD, Shenzhen, China. The PAC has a stated specific surface area of  $900 \text{ m}^2\cdot\text{g}^{-1}$  and total pore volume of  $0.6 \text{ cm}^3\cdot\text{g}^{-1}$ . The general properties of the four isothiazolones are listed in Table S1. Methanol (high-performance liquid chromatography (HPLC) grade) was purchased from J.T. Baker (Avantor Performance Materials Inc., USA). A Milli-Q purification system (Millipore, UK) was employed to produce ultra-pure water

(resistivity  $\geq 18.2 \text{ M}\Omega\cdot\text{cm}$ ). All other chemical reagents were of analytical grade. The ROC used in this study was obtained from the reverse osmosis system of a dyeing factory (Foshan, China).

## 2.2. Adsorption Experiments

Adsorption experiments were carried out using batch experiments. To measure the kinetics, 20-mL aliquots of aqueous solutions containing an isothiazolone biocide were placed in 30-mL vials and agitated in a constant temperature incubator shaker at 100 rpm and  $298 \pm 1 \text{ K}$  with  $100 \text{ mg}\cdot\text{L}^{-1}$  PAC that was diluted from a  $5 \text{ g}\cdot\text{L}^{-1}$  stock solution. The PAC dose was determined based on cost considerations for practical applications. Specific amounts of the adsorption solutions were sampled and filtered through  $0.22 \mu\text{m}$  filters for analysis at predetermined times. Agitation was maintained for 48 h for the adsorption isotherm experiments, by which time the adsorption equilibrium had almost been attained (Figure S1). The amount of isothiazolone taken up, and the removal of the biocides by the adsorbent, were calculated using the following equations:

$$q = \frac{(C_0 - C) \times V}{M} \quad (1)$$

$$\text{Removal} = \frac{(C_0 - C)}{C_0} \times 100\% \quad (2)$$

where  $q$  is the amount of isothiazolone taken up by the adsorbent ( $\text{mg}\cdot\text{g}^{-1}$ ),  $C_0$  is the initial concentration of isothiazolone before adsorption ( $\text{mg}\cdot\text{L}^{-1}$ ), and  $C$  is the concentration of isothiazolone after adsorption ( $\text{mg}\cdot\text{L}^{-1}$ ).

The partition coefficient  $K_d$ , which is described by the following equation, was used to evaluate the effects of pH:

$$K_d = \frac{(C_0 - C) \cdot V}{M \cdot C_0} \quad (3)$$

where  $V$  is the solution volume (L) and  $M$  is the adsorbent mass (g).

## 2.3. Analysis of Isothiazolone Concentrations

The concentrations of isothiazolones were measured using an HPLC (LC-20AD, Shimadzu, Japan) system with a Venusil MP-C18 reverse-phase column ( $4.6 \times 250 \text{ mm}$ ,  $5 \mu\text{m}$  particles, Bonna Agela Technologies, USA) and an ultraviolet (UV) absorbance detector (SPD-M20A, Shimadzu, Japan). The operation conditions are listed in Table S2.

## 2.4. Point of Zero Charge Determination

The point of zero charge (PZC) of PAC was measured using the batch equilibrium method [22]. Briefly, samples of PAC (0.2 g) were shaken in a series of 100 mL conical flasks with 50 mL of  $0.01 \text{ mol}\cdot\text{L}^{-1}$  NaCl at different pH values for 48 h, which was sufficient to achieve adsorption equilibrium. Initial pH values were adjusted using NaOH and HCl, and the final pH was measured after adsorption. The point at which the initial and final pH were the same is the point of zero charge ( $\text{pH}_{\text{PZC}}$ ).

## 2.5. Adsorption Kinetics Models

The pseudo first-order model is used to describe the adsorption of a solute from a solution [23]:

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

where  $q_e$  ( $\text{mg}\cdot\text{L}^{-1}$ ) and  $q_t$  ( $\text{mg}\cdot\text{L}^{-1}$ ) are the amounts of isothiazolone adsorbed at equilibrium and at time  $t$  (min) respectively, and  $k_1$  is the rate constant of adsorption ( $1\cdot\text{min}^{-1}$ ). The values of  $k_1$  and  $q_e$  can be calculated from a plot of  $q_t$  versus  $t$ .

The second-order kinetic model is expressed as follows [24]:

$$t/q_t = 1/k_2q_e^2 + t/q_e \quad (5)$$

where  $k_2$  ( $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ ) is a constant related to the adsorption rate.

## 2.6. Adsorption Isotherm Models

The *Langmuir* and *Freundlich* models were used to simulate the adsorption isotherms. The *Langmuir* model assumes monolayer adsorption in which a single adsorbate binds to a single adsorption site of a homogeneous surface. The *Freundlich* model assumes a heterogeneous surface with non-uniform adsorption energy [25].

The *Langmuir* isotherm is expressed by the following equation:

$$C_e/q_e = 1/q_m k_L + C_e/q_m \quad (6)$$

where  $C_e$  ( $\text{mg} \cdot \text{L}^{-1}$ ),  $k_L$  ( $\text{L} \cdot \text{g}^{-1}$ ), and  $q_m$  ( $\text{mg} \cdot \text{g}^{-1}$ ) are the equilibrium concentration of isothiazolone, the *Langmuir* constant, and the predicted adsorption capacity respectively.

The *Freundlich* isotherm is expressed by the following equation [26]:

$$q_e = k_F \cdot C_e^{1/n} \quad (7)$$

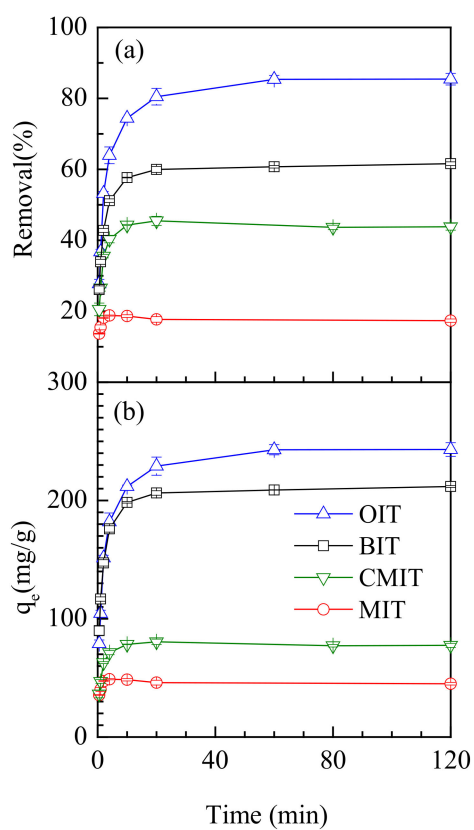
where  $k_F$  is the *Freundlich* constant and  $n$  is the number of adsorption sites.

## 3. Results and Discussion

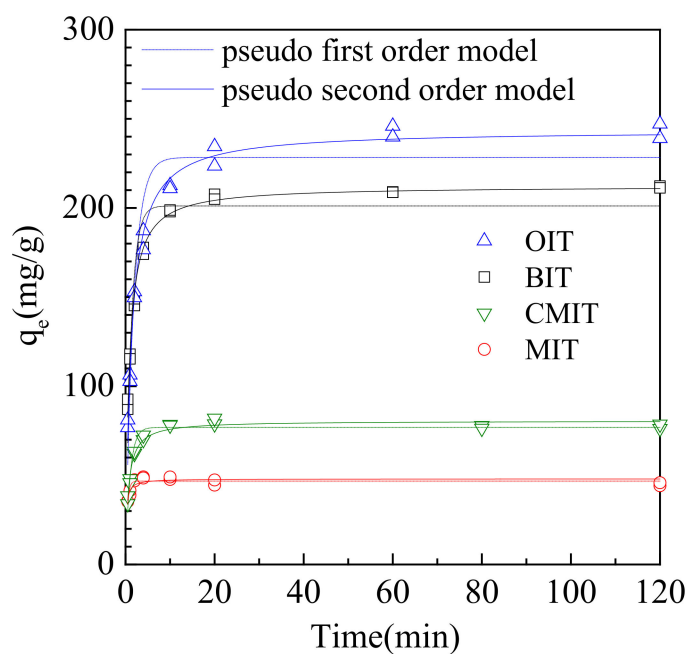
### 3.1. Adsorption Rate and the Elimination of Isothiazolone by PAC

Adsorption kinetics experiments were conducted with initial isothiazolone concentrations of 15–35  $\text{mg} \cdot \text{L}^{-1}$ . Figure 1 shows the isothiazolone adsorption on PAC over time. The removal percentages of different isothiazolones varied during the first 20 min, after which they stabilized, indicating that an equilibrium state was being approached. PAC normally reaches equilibrium quickly, while adsorption of imidacloprid [27] and DOC [28] approach equilibrium during the first 30 min. The removal of the isothiazolones occur in the following order: OIT (85%) > BIT (62%) > CMIT (44%) > MIT (17%), which correspond to adsorption amounts of OIT ( $243 \text{ mg} \cdot \text{L}^{-1}$ ) > BIT ( $212 \text{ mg} \cdot \text{L}^{-1}$ ) > CMIT ( $77 \text{ mg} \cdot \text{L}^{-1}$ ) > MIT ( $45 \text{ mg} \cdot \text{L}^{-1}$ ).

The kinetics of isothiazolone adsorption onto PAC were simulated by the pseudo first-order model and the pseudo second-order model (Figure 2); fitting parameters are presented in Table 1. The kinetics were described slightly better by the pseudo second-order model than by the pseudo first-order model. Except for MIT, the adsorption of isothiazolones onto PAC fit the second-order kinetic model well, with a regression squared residual ( $R^2$ ) > 0.97. Similarly, second-order kinetic models have been found to be suitable for describing the adsorption of imidacloprid [27], pentafluorophenol [18], and dye [29]. For MIT, the adsorption equilibrium was reached in a short time. Low molecular weight DOMs reportedly take less time to be adsorbed than high molecular weight organics, because of their shorter diffusion time through the carbon pores of PAC [28]. Because of the rapidly reached adsorption saturation and the possible existence of desorption for MIT, the model results of MIT were not in good agreement with the data. Therefore, it is possible that neither model was appropriate to describe the MIT adsorption onto PAC.



**Figure 1.** Effect of adsorption time on the removal of isothiazolones (a) and adsorption amounts (b) at 298 K with a PAC dose of 100 mg·L<sup>-1</sup>.



**Figure 2.** Kinetic adsorption curves for isothiazolones at 298 K on PAC.

**Table 1.** Parameters calculated from kinetic models.

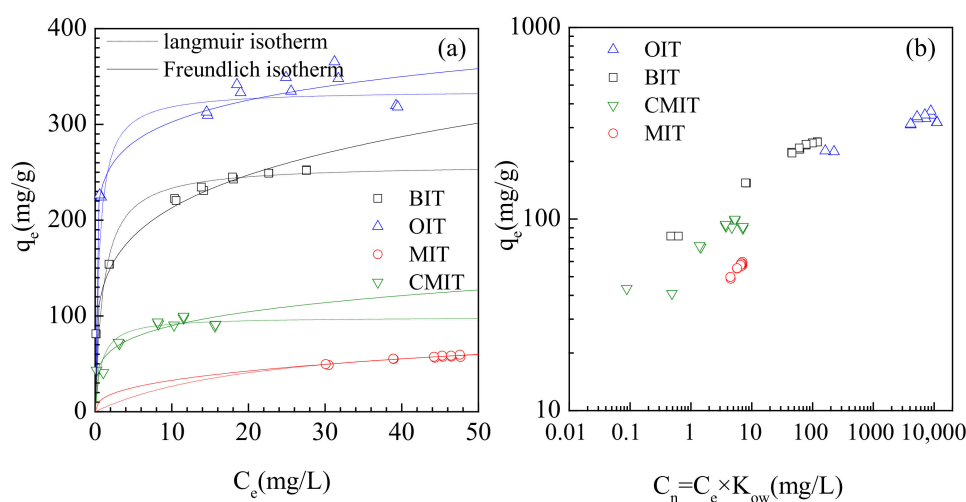
| Kinetic Model             | Parameter  | MIT   | CMIT  | BIT   | OIT    |
|---------------------------|--|-------|-------|-------|--------|
| pseudo first order model  | $K_1(1 \cdot \text{min}^{-1})$                             | 2.58  | 0.996 | 0.829 | 0.565  |
|                           | $q_e(\text{mg} \cdot \text{g}^{-1})$                       | 46.8  | 76.9  | 201   | 228    |
|                           | $R^2$  | 0.795 | 0.945 | 0.911 | 0.930  |
| pseudo second order model | $K_2(\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1})$ | 0.129 | 0.020 | 0.006 | 0.0033 |
|                           | $q_e(\text{mg} \cdot \text{g}^{-1})$                       | 48.0  | 80.5  | 212   | 244    |
|                           | $R^2$  | 0.749 | 0.971 | 0.992 | 0.990  |

According to the parameter  $K$  of the two models, the adsorption rates followed an order of MIT > CMIT > BIT > OIT, while adsorption amounts followed an opposite order of OIT > BIT > CMIT > MIT. The strong adsorption capacity and low adsorption rate of OIT indicates that diffusion may be the main contributor to adsorption [14].

### 3.2. Equilibrium Adsorption

#### 3.2.1. Adsorption Isotherms

Figure 3a shows the adsorption isotherms of the four isothiazolone biocides on PAC at 298 K over a concentration range of 0–50  $\text{mg} \cdot \text{L}^{-1}$ . The fitting parameters are presented in Table 2. The results showed that the adsorption of isothiazolones onto PAC fit both the *Langmuir* and *Freundlich* models well ( $R^2 > 0.92$ ). The fit for the *Langmuir* model was >0.98, indicating that the *Langmuir* model is ideal for simulating the adsorption of isothiazolones. It has been reported that the *Langmuir* model fits the adsorption of methylene [30], Direct Blue 2B and Direct Green B dyes [29] on activated carbon. The *Freundlich* model has also been used to simulate the adsorption of tannic acid, 4-chlorophenol and phenol onto KOH-activated carbons [31].



**Figure 3.** Adsorption isotherm curves of isothiazolones on PAC (a) and hydrophobicity ( $K_{ow}$ ) modified adsorption isotherm curves (b). Conditions: shaking frequency 100 rpm, temperature 298 K, pH = 7.

The adsorption amounts followed the order OIT > BIT > CMIT > MIT, which is in accordance with their octanol/water partition coefficients ( $K_{ow}$ ). These findings suggested that the hydrophobicity of the isothiazolones played a key role in the adsorption amounts. A large proportion of the hydrophobic OIT and BIT were adsorbed. The  $K_{ow}$  was used to normalize the aqueous concentrations ( $C_n = C_e \times K_{ow}$ ) to eliminate the differences caused by the hydrophobicity of isothiazolones [14,19]. After normalization,

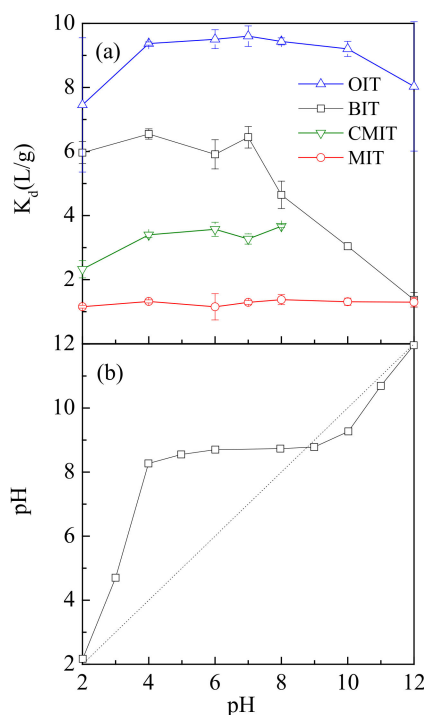
$q_e$  and  $C_n$  had a linear relationship in a Log-linear form (Figure 3b), indicating that the hydrophobicity of the isothiazolones was the main factor for adsorption onto PAC.

**Table 2.** Parameters calculated from isotherm models.

| Equilibrium Model   | Parameters                         | MIT   | CMIT  | BIT   | OIT   |
|---------------------|------------------------------------|-------|-------|-------|-------|
| Langmuir isotherm   | $K_L(\text{L}\cdot\text{g}^{-1})$  | 0.04  | 1.24  | 0.93  | 1.83  |
|                     | $q_m(\text{mg}\cdot\text{g}^{-1})$ | 86.3  | 98.6  | 258   | 336   |
|                     | $R^2$                              | 0.989 | 0.994 | 0.999 | 0.997 |
| Freundlich isotherm | $K_F$                              | 13.7  | 54.4  | 129   | 237   |
|                     | $n$                                | 2.65  | 4.62  | 4.63  | 9.52  |
|                     | $R^2$                              | 0.973 | 0.924 | 0.997 | 0.946 |
| $\log K_{ow}$       |                                    | −0.83 | −0.34 | 0.64  | 2.45  |

### 3.2.2. pH Effect

The solution pH exerts a profound effect on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecules [29]. In the present study, this effect was investigated using a pH range of 2 to 12 (Figure 4a) and initial isothiazolone concentrations of  $30 \text{ mg}\cdot\text{L}^{-1}$ . The adsorption efficiency followed the order of  $\text{OIT} > \text{BIT} > \text{CMIT} > \text{MIT}$ , which was similar to the order of the isotherms. Notably, CMIT decomposed under alkaline conditions.



**Figure 4.** Effect of pH on the adsorption of isothiazolones onto  $100 \text{ mg}\cdot\text{L}^{-1}$  PAC dose (a) and determination of  $\text{pH}_{\text{PZC}}$  (b).

The  $K_d$  values of MIT adsorption remained around  $1 \text{ g}\cdot\text{L}^{-1}$  over the pH range, implying that the functional groups have a limited effect on MIT adsorption.

The  $K_d$  values of BIT adsorption increased with pH from 2 to 4. PAC was positively charged in this range, and only a small fraction of BIT remained in an ionic state at pH 2. As pH increased, the charges of functional groups decreased, weakening repulsive forces to BIT, with  $\text{BIT}^+$  turning into BIT at the same time. These changes explained the increase in  $K_d$  values. As pH increased from 7 to 12,  $K_d$  values



decreased from  $6 \text{ g}\cdot\text{L}^{-1}$  to  $1 \text{ g}\cdot\text{L}^{-1}$ , and the ideal pH was far lower than the  $\text{pH}_{\text{PZC}}$  ( $\text{pH}_{\text{PZC}} = 8.77$ ). This is because BIT may ionize at high pH, resulting in its becoming hydrophilic. Excess  $\text{OH}^-$  may also compete with BIT for PAC adsorption sites under alkaline conditions. Therefore, the  $K_d$  values of BIT reached  $1 \text{ g}\cdot\text{L}^{-1}$  when the pH was 12, which was equivalent to the values of MIT. Similarly, this phenomenon occurred for the adsorption of mc-LR and pentafluorophenol in some previous studies, where the solid-phase concentration decreased as pH increased beyond the  $\text{pK}_a$ , because the anionic forms of mc-LR, which are found at high pH, are not well adsorbed [18,32].

The states of BIT under different pH conditions according to its  $\text{pK}_a$  are shown in Figure 5. The state of BIT was type (b) at pH 2–6, which was non-ionic and hydrophobic, resulting in high adsorption. The BIT held a negative charge when the pH was 7–12, which meant that it had a tight affinity with water and was poorly adsorbed by PAC.

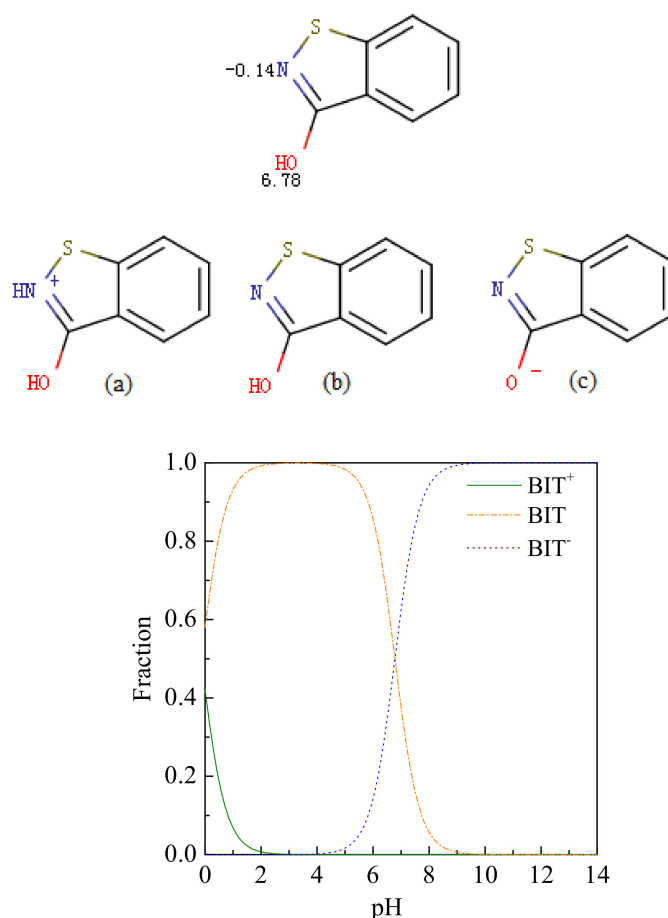


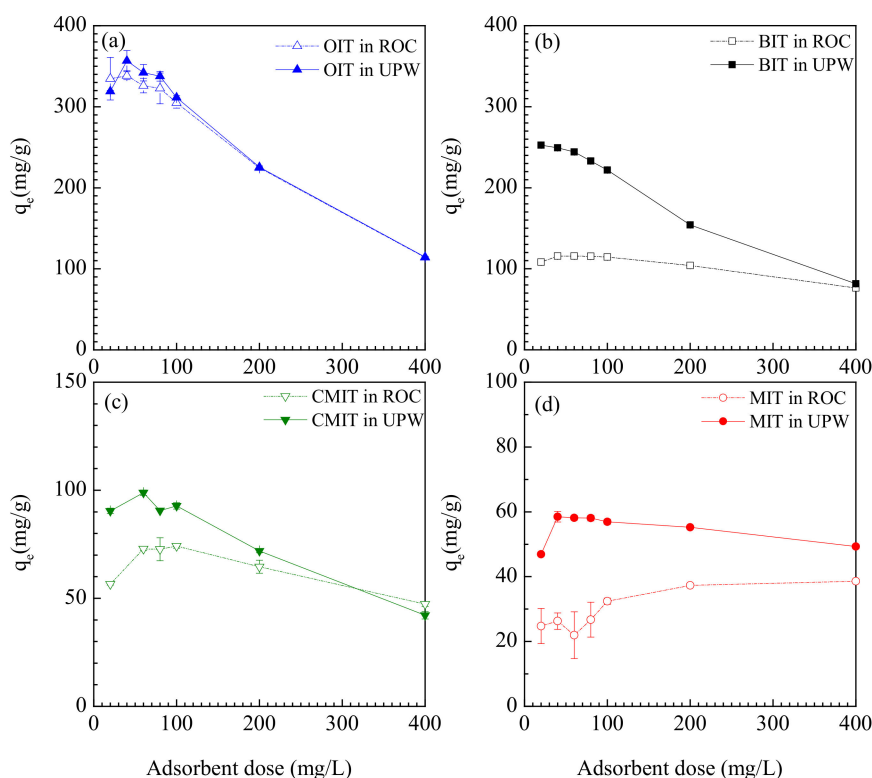
Figure 5. Influence of pH on the fraction of charging states of BIT.

The OIT had charged functional groups when the pH was  $<4$ , which influenced the adsorption. At  $\text{pH} > \text{pH}_{\text{PZC}}$ , the negatively charged oxygen functional groups also impeded the adsorption of OIT onto PAC. The functional groups also influence the adsorption of reactive Red M-2BE [33].

### 3.2.3. Effect of Textile Reverse Osmosis Concentrate

The isothiazolones were diluted in textile ROC with a TOC of  $29 \text{ mg}\cdot\text{L}^{-1}$  at the same biocide concentrations as were used in the ultra-pure water (UPW) experiments to further evaluate the feasibility of applying PAC for isothiazolone adsorption in real practice. There was no substantial change in adsorption amount between the two solutions for OIT (Figure 6a), showing that the organics in the ROC occupied few of the hydrophobic adsorption sites that bind OIT.





**Figure 6.** Effects of textile reverse osmosis concentrate on the amount of isothiazolones adsorbed. OIT (a), BIT (b), CMIT (c) and MIT (d). Note: ROC, reverse osmosis concentrate; UPW, ultra-pure water.

For BIT (Figure 6b) and CMIT (Figure 6c), the  $q_e$  values in ROC were markedly lower than those in UPW when the PAC dose was under  $100 \text{ mg} \cdot \text{L}^{-1}$ . Dissolved hydrophobic organics in the ROC compete for adsorption sites with BIT and CMIT, and this competition decreased the adsorption capacity for these isothiazolones. The adsorption of neutral and dissociated species, such as polar 2,4-dichlorophenol and 4-chloroaniline, on multiwalled carbon nanotubes can be mutually suppressed by nonpolar naphthalene [34]. The amounts of BIT and CMIT adsorbed decreased substantially in ROC at low PAC dosages as there were insufficient adsorption sites for the isothiazolones. When there were sufficient adsorbent and adsorption sites, the differences between ROC and UPW diminished, with little effect from the ROC on the adsorption amounts of BIT and CMIT being observed at an adsorbent dose of  $400 \text{ mg} \cdot \text{L}^{-1}$ . Structural fractions of DOM make an important contribution to the adsorption of relatively polar organic pollutants by carbon materials. For example, the hydrophobic fractions of the DOM decreased carbamazepine adsorption, while the hydrophilic fractions exhibited negligible effects [35].

The amount of MIT adsorbed in ROC was much lower than that in UPW, even when the PAC dose was  $400 \text{ mg} \cdot \text{L}^{-1}$  (Figure 6d). MIT is hydrophilic; therefore, it does not easily adhere to the surface of PAC when competing with organics in ROC. Non-organic matter decreased the  $q_m$  of microcystin-LR, which had similar adsorption characteristics to MIT on activated carbon [32].

#### 4. Conclusions

In this study, different kinds of isothiazolones were investigated. The results suggest that the adsorption of isothiazolones by PAC is a feasible and effective method for the treatment of ROC containing isothiazolone biocides.

The *Langmuir* isotherm suits the isothiazolone adsorption isotherms better than the *Freundlich* isotherm. Adsorption amounts are consistent with the  $K_{ow}$  of the isothiazolones, with an order of

OIT > BIT > CMIT > MIT. Large amounts isothiazolones with a high  $K_{ow}$  are easily adsorbed and hydrophilicity is the main factor influencing PAC adsorption.

The pH can influence the adsorption of isothiazolones, mainly because the form of the isothiazolones varied at different pH values. Actual textile ROC has no effect on the adsorption of OIT, while the ROC decreased the adsorption capacity for BIT, CMIT and MIT. Based on these findings, it can be concluded that these isothiazolones compete with organics for adsorption sites.

Further research focusing on surface modification of carbon materials for adsorption of hydrophilic pollutants, and an efficient regeneration process is proposed for application of PAC treatment of ROC.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4441/10/4/532/s1>, Figure S1: Effect of adsorption time on BIT adsorption amounts, Table S1: General properties of the four isothiazolones.

**Author Contributions:** Bing-Tian Li, Qian-Yuan Wu and Zhuo Chen conceived and designed the experiments; Ang Li contributed experimental method; Bing-Tian Li performed the experiments; Qian-Yuan Wu, Bing-Tian Li, Zhuo Chen and Wen-Long Wang analyzed the data under the supervision of Hong-Ying Hu; Tian-Hui Zhou and Ying-Xue Sun helped in editing and improving the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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