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**Magnetic activated carbon prepared from rice straw-derived hydrochar
for triclosan removal**

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Recently, considerable attention has been received in the hydrothermal liquefaction (HTL) of waste rice straw for the production of bio-oil and hydrochar. However, hydrochar material could not be directly applied in the environmental field, due to its limited porosity and surface area. In order to improve the porosity and adsorption capacity of rice straw-derived hydrochar, it was activated and magnetized to a magnetic activated carbon. The activation condition for hydrochar was firstly considered, due to the negative effect of magnetic medium. Results suggested that the as-prepared magnetic activated carbon possessed a large surface area (around $674 \text{ m}^2 \text{ g}^{-1}$), and exhibited both high adsorption capacity and fast adsorption rate for triclosan (TCS) removal. In addition, magnetic activated carbon can be easily recovered from aqueous solutions by an external magnetic field. Overall, the waste rice straw-derived hydrochar can be transformed to a highly efficient magnetic adsorbent for TCS removal.

1. Introduction

Triclosan (TCS, 5-chloro-2-(2,4-dichlorophenoxy)-phenol), a widely used antimicrobial agent in pharmaceuticals and personal care products (PPCPs), has been received widespread public attention, due to its frequent detection in surface waters and its potential risk to human health.^{1,2} It is reported that TCS is toxic to aquatic organisms, and contributes to the generation of more toxic by-products like dioxin.^{3, 4} Hence, it is of great importance to explore efficient and cost-effective treatment technologies for TCS removal from aqueous solution.

Rice straw is an abundant agriculture residue and utilized to produce bio-oil and hydrochar *via* hydrothermal liquefaction (HTL).⁵⁻⁷ However, to date, more attention are focused on the production of bio-oil, with less attention paid to hydrochar.^{8, 9} Rice straw-derived hydrochar is also an attractive carbon material, due to abundant oxygen-contained functional groups on its surface.^{10, 11} However, the limited porosity and low surface area of hydrochar restrict the effective exploitation in environmental remediation and agricultural application.¹²⁻¹⁴ Hence, rice straw-derived hydrochar is needed to be modified for the development of porosity.

It has been previously reported that the resultant carbons from chemical activation of hydrochar by activating agents (KOH, H₃PO₄ or ZnCl₂), possess large surface area and abundant pore structure.¹⁵⁻¹⁷ However, little information about hydrochar activated by potassium carbonate (K₂CO₃) has been reported. K₂CO₃, a porogen with widespread application, can also activate waste carbonaceous materials to a high-porosity activated carbon, which is strongly dependent on the suitable K₂CO₃ impregnation ratio and activation temperature.¹⁷ However, activated

carbon is difficult to be separated and recovered from aqueous solutions. Therefore, it is of great importance to employ an efficient and cost-effective technology to deal with the issue.

Generally, introducing magnetic medium to waste biomass, activated carbon or carbon nanotubes *via* hydrothermal co-precipitation reaction of ferrous and ferric ions under basic solution is a facile method to enable carbonaceous material to be efficiently separated from aqueous solutions. Nevertheless, only the magnetic carbon composite prepared from a high porosity carbonized material can retain high porosity, due to the pore-jamming effect of magnetic medium.¹⁸⁻²⁰ Then, the performance of porous structure and surface area of magnetic carbon composite is closely related to its precursor. Therefore, the optimization of activation conditions for the precursor of magnetic carbon composite should be firstly considered.

In this study, a novel magnetic activated carbon with developed porosity and high adsorption capacity has been prepared from waste rice straw-derived hydrochar via two steps. In order to enable magnetic activated carbon to possess a large surface area, the activation conditions for its precursor are firstly optimized. The main objectives of this research are to investigate the evolution of textural properties and surface chemistry between rice straw-derived hydrochar and its activated material, and to evaluate the application of the as-prepared magnetic activated carbon in TCS removal. In order to elucidate the pore-jamming effect of magnetic composition, the performances of activated carbon are also studied. It should be emphasized that few reports have been devoted to the preparation of magnetic activated carbon using this precursor.^{10, 12, 13, 21}

2. Experimental

2.1 Materials

Analytical grade anhydrous potassium carbonate (K_2CO_3) and triclosan (TCS) were purchased from Sinopharm Chemical Reagent Co. Ltd. and Aladdin Reagent Corporation, respectively. Ultrapure water was generated from a Milli-Q academic water purification system (Millipore) with a resistivity of $18.2\text{ M}\Omega\text{ cm}^{-1}$.

The rice straw-derived hydrochar material was obtained from our pilot-scale HTL unit. The HTL unit was performed using a hydrothermal reaction system (shown in Fig. S1), which consisted of a pilot-scale stainless steel autoclave, an electrically heated furnace, a magnetic stirrer, a pressure holding circuit and a controller. In a typical experimental run, 3.5 kg of rice straw and 44 L of water were placed in the autoclave and heated up to 573 K and maintained at this temperature for 30 min, followed by cooling to room temperature. The resulting solid product, denoted as hydrochar, was collected by filtration and washed with abundant ethyl acetate and distilled water, and finally dried for 4 h at 373 K.

2.2 Fabrication of magnetic activated carbon

The synthesis process of magnetic activated carbon was divided into two steps as follows: (1) fabrication of activated carbon *via* chemical activation of rice straw-derived hydrochar by K_2CO_3 ; (2) fabrication of magnetic activated carbon *via* the hydrothermal co-precipitation reaction. More details about the preparation process of activated carbon and magnetic activated carbon can be available in Supporting Information.

2.3 Characterization

The Brunauer-Emmett-Teller (BET) surface areas of samples were obtained from nitrogen adsorption isotherms at 77 K using a Quantasorb SI instrument (Quantachrone, USA). The X-ray diffraction (XRD) was carried out on the X'Pert PRO system equipped with a Cu K α radiation (40 kV, 40 mA) over the 2θ range of 20-70°. The X-ray photoelectron spectroscopy analysis (XPS) were performed using a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K α radiation ($h\nu = 1253.6$ eV), and binding energies for the high-resolution spectra were calibrated by setting C 1s at 284.6 eV. To investigate the surface properties of as-prepared samples, the Fourier transform infrared (FT-IR) spectra were recorded in the region of 4000-400 cm^{-1} employing the KBr pellet method (Nexus 470, Nicolet). The microscopic features of samples were characterized by scanning electron microscopy (SEM, XL300, Philips) equipped with an energy-dispersive X-ray (EDX, Link 300) analyzer and transmission electron microscopy (TEM, H-600, Hitachi). The magnetic property was investigated using a vibrating sample magnetometer (VSM, Quantum).

2.4 Batch adsorption experiments

Adsorption performance of TCS on activated carbon and magnetic activated carbon were compared, in order to interpret the negative effect of magnetic composition. Batch adsorption equilibrium experiments were carried out in a set of 60 mL amber glass bottles, containing TCS solutions (20 % HPLC-grade methanol) with different initial concentrations (10 - 50 mg L^{-1}) and adsorbent (50 mg L^{-1}) on a shaker at 298 K. Adsorption kinetics of TCS onto adsorbents were performed with the initial TCS concentration of 10, 20 and 40 mg L^{-1} , respectively. After shaken

continuously under certain time, the solid adsorbent was separated from solutions by centrifugation. Then the mixture of 1 mL obtained supernatant and 1 mL methanol was filtrated by 0.45 μm polytetrafluoroethylene (PTFE) membrane filters. The amount of adsorption at equilibrium (q_e , mg g^{-1}) was calculated using the following equation (equation 1):

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

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentration of TCS, respectively. V (L) is the volume of the solution, and m (g) is the mass of adsorbent.

The effect of real water was studied under initial TCS concentrations of 20 mg L^{-1} in different water matrix (sea water, lake water, ground water, river water and pure water). The total organic carbon (TOC) of the real water was determined with a Shimadzu TOC-L analyzer. And the effect of pH on TCS adsorption was investigated in aqueous solutions over a pH range of 3-10 at initial TCS concentration of 20 mg L^{-1} .

2.5 HPLC analysis

The TCS concentrations were determined by an Agilent 1100 HPLC with a Zorbax ODS column ($4.6 \text{ mm} \times 150 \text{ mm}$) at 298 K . The wavelength of ultraviolet detector was set at 280 nm , and the injection volume was $50 \mu\text{L}$. The mobile phase was a mixture of HPLC-grade methanol and ultrapure water (90:10, v/v), which was delivered at 1 mL min^{-1} through the column.

3. Results and discussions

3.1 Optimization of activation conditions

In order to obtain a high-performance magnetic activated carbon, the optimization of

activation conditions for rice straw-derived hydrochar was firstly considered. Fig. S2 and S3 exhibit nitrogen gas (N_2) adsorption isotherms of activated carbons prepared under various activation temperature and impregnation ratio (the weight ratio of K_2CO_3 to hydrochar). According to the IUPAC classification, N_2 adsorption isotherms of these activated carbons exhibit a combination of type I and IV, indicating the characteristics of microporous and mesoporous structures.

As shown in Table 1, the yield of activated carbons decreased from 57.0% to 21.1% as the activation temperature increased from 773 to 1073 K, due to the release of volatile products as a result of intensifying dehydration and elimination reaction.²² Accordingly, with increasing the activation temperature, the BET surface area and the micropore surface area sharply increased from 308 to 909 $m^2 g^{-1}$ and from 256 to 654 $m^2 g^{-1}$, respectively, due to the release of tars from the cross-linked framework generated by treatment of the chemical reagents.¹⁷ Therefore, the total volume and micropore volume was obviously increased. However, the proportion of micropore surface area and micropore volume gradually increased before 973 K, and then decreased, partly due to the enlarging of existing micropores into mesopores.²³ Therefore, violent gasification reactions occurred and decreased the microporosity at activation temperature of 1073 K.

The influence of the impregnation ratio on the characteristics of activated carbons was also investigated at activation temperature of 873 K. The BET surface area, total volume and micropore volume obviously increased with increasing impregnation ratio, and the proportion of

the micropores to the total pore volume remained steady, as indicated in Table 1.

3.2 Characterization of samples

In this study, the activated carbon with activation temperature 1073 K and impregnation ratio 2:1 was selected to prepare magnetic activated carbon, due to its high porosity. The N₂ adsorption isotherms and pore size distributions for hydrochar, activated carbon and magnetic activated carbon are shown in Fig. S4. Obviously, hydrochar exhibited Type III isotherm, suggesting that rice straw-derived hydrochar possessed less developed porous structure. After activation, the isotherms for activated carbon and magnetic activated carbon presented a combined feature of type I and IV curves, indicating the existence of both micropores and mesopores.

As shown in Table 2, hydrochar presented extremely low BET surface area ($6.22 \text{ m}^2 \text{ g}^{-1}$) and total pore volume ($0.06 \text{ cm}^3 \text{ g}^{-1}$). Compared with hydrochar, a remarkable increase in BET surface area and pore volume (including total pore and micropore) was observable for activated carbon and magnetic activated carbon, further demonstrating the importance of activation in the development of pore structure. Furthermore, compared with activated carbon, the surface area of magnetic activated carbon reduced from 1334 to $674 \text{ m}^2 \text{ g}^{-1}$, indicating the negative effect of magnetic medium. At the same time, it was found that 48.6% and 52.0% of total pore volume and micropore volume, respectively, were diminished after precipitation of iron particles, indicating the formation of iron particles inside the pore structure of activated carbon.²⁴

The structure and chemical composition of the samples were determined by XRD. As seen in

Fig. 1a, the major crystalline phases for rice straw-derived hydrochar were quartz (SiO_2), weddellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) and whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$). After activation, XRD peaks corresponding to different phases of calcite (CaCO_3) appeared in activated carbon, which can be attributed to the decomposition of weddellite and whewellite at high activating temperature. After magnetization, magnetic medium, such as goethite (peaks at $2\theta = 21.2$ and 35.5°), maghemite (peaks at $2\theta = 35.5$, 40.5 , 44.6 , 53.1 and 57.4°) and magnetite (peaks at $2\theta = 35.5$ and 61.3°), were identified as the major crystalline phase in the magnetic activated carbon.²⁵ To obtain further information in the surface composition for magnetic activated carbon, XPS analysis was carried out. The C 1s and O 1s spectra of magnetic activated carbon are shown in Fig. 1b and c, and the relative peak areas of C and O in different forms on the surface of magnetic activated carbon are presented in Table S1.^{26, 27} It was obvious that the main functional groups containing C were C-C (284.6 eV) and O-C=O (289.0 eV). In addition, it can be deduced from the curve fitting results of O 1s spectra that, the composition ratio of magnetite (Fe_3O_4), goethite ($\text{FeO}(\text{OH})$) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) was 1:2.5:1, further reflecting the presence of iron particles on the surface of carbon materials.

Fig. 1d compares the evolution of FT-IR spectra for hydrochar, activated carbon and magnetic activated carbon samples. The wide band 3400 cm^{-1} , visible for all samples, can be attributed to the -OH stretching vibrations.²¹ Moreover, all samples displayed the similar adsorption band with various intensities, due to partial oxygen and carbon removal. The band at $2924/2854$, $1587/1449$, 1080 and 797 cm^{-1} , which were assigned to C-H stretching vibrations, skeletal C=C

183 vibrations, C-O bonds stretch, and out-of-plane deformation vibrations of C-H groups,
184 respectively.¹ However, the peak at 455 cm^{-1} , assigned to the stretching vibration of Si-O-Si
185 groups in the quartz, was only observable in hydrochar and activated carbon, but disappeared in
186 magnetic activated carbon, which was in good agreement with the results of XRD analysis.
187 Accordingly, magnetic activated carbon exhibited an additional band at 583 cm^{-1} , compatible
188 with the presence of iron oxide in the sample.¹⁹

189 Details about the structure and morphology of the obtained samples were examined in the
190 SEM and TEM observations (shown in Fig. 2). The surface of hydrochar appeared rough, with
191 rarely rudimentary pores due to the preliminary constitute decomposition (Fig. 2a).¹⁸ After
192 activation, numerous surface pores were produced, contributing to the increase of the surface
193 area (Fig. 2b).⁴ Further magnetization, the iron oxide or hydroxide particles covered the surface
194 of activated carbon, blocking the pores (Fig. 2c).²⁸ These results well agree with the data of
195 surface areas from Table 2. And the TEM images confirmed that developed porosity was formed
196 in activated carbon, compared with hydrochar (Fig. 2d, e).

197 To evaluate the magnetic behavior of magnetic activated carbon, the magnetic measurements
198 were carried out at 300 K. According to hysteresis loop (Fig. S5), the saturation magnetization of
199 magnetic activated carbon was measured to be 12.4 emu g^{-1} , indicating a superparamagnetic
200 behavior. This implied that magnetic activated carbon can be easily recovered by an external
201 magnetic field (Fig. S5, inset), thus providing a potential advantage for the separation of
202 adsorbents.²⁴

3.3 Adsorption studies

3.3.1 Adsorption isotherms

Adsorption isotherm is basically important to describe how adsorbates interact with adsorbents, and is critical in optimizing the use of adsorbents. In this study, two widely used isotherm models (the Langmuir model and Freundlich model) were employed to describe the adsorption process. The Langmuir model (Eq. (2)) and Freundlich model (Eq. (3)) can be represented as follows:

$$C_e/q_e = 1/q_m K_L + C_e/q_m \quad (2)$$

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (3)$$

where q_m is the maximum adsorption capacity (mg g^{-1}), K_L is a constant related to free energy or adsorption enthalpy (L mg^{-1}), K_F is related to the adsorption capacity of the adsorbent ($\text{mg}^{(1-1/n)} \text{g}^{-1} \text{L}^{1/n}$), and $1/n$ is another constant related to the surface heterogeneity.

The Langmuir and Freundlich parameters, together with regression coefficients, in adsorption of TCS onto activated carbon and magnetic activated carbon are listed in Table 3. As indicated in Fig. S6, the adsorption of TCS onto activated carbon and magnetic activated carbon was well fitted with Langmuir model, in accordance with the correlation coefficient (R^2) values obtained from Table 3. It was evident that the adsorption capacity of TCS on activated carbon, was significantly greater than that on magnetic activated carbon, indicating that the adsorption process was mainly dependent upon surface area and porosity of adsorbents and further demonstrating the negative effect of magnetic medium.²⁹ Compared with the TCS adsorption capacities of various previously known adsorbents (Table S2), magnetic activated carbon

221 exhibited an excellent adsorption performance.^{1, 3, 30, 31}

222 For the Langmuir model, to determine whether the adsorption system is favorable or not, the
223 isotherm can be classified by the separation factor (R_L), which is represented by the following
224 equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

225 The value of K_L is listed in Table 3. The R_L parameter gives important signs on the possibility
226 of the adsorption process that might be irreversible ($R_L=0$), favorable ($0 < R_L < 1$), linearity of
227 adsorption ($R_L=1$) or unfavorable ($R_L > 1$). In the present work, the R_L values were found within
228 the range of 0.02-0.04, demonstrating that TCS adsorption onto activated carbon and magnetic
229 activated carbon was favorable.

230 3.3.2 Adsorption kinetics

231 In order to investigate the rate of TCS adsorption, three different kinetic models, i.e. the
232 pseudo first-order model (Eq. (5)), pseudo second-order model (Eq. (6)) and Elvoich equation
233 (Eq. (7)),³² were applied to simulate the kinetics of TCS adsorption onto activated carbon and
234 magnetic activated carbon.

$$q_t = q_e (1 - e^{-k_1 t}) \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

$$q_t = \left(\frac{1}{b}\right) \ln(ab) + \left(\frac{1}{b}\right) \ln t \quad (7)$$

235 where q_t is the amount of TCS adsorbed at time t (mg g^{-1}); k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the
236 pseudo first-order and pseudo second-order rate constant, respectively; a is the initial adsorption

rate constant ($\text{mg g}^{-1} \text{min}^{-1}$) and b is related to the extent of surface coverage and activation energy for chemisorption (g mg^{-1}).

The adsorption kinetics parameters are listed in Table 4. Obviously, the pseudo second-order equation agreed well with the data for $R^2 \geq 0.99$. Additionally, the $q_{\text{e,cal}}$ from pseudo second-order model were close to the experimental values $q_{\text{e,exp}}$. Therefore, the pseudo second-order model was the best for predicting the adsorption kinetics of TCS onto activated carbon and magnetic activated carbon.

As shown in Fig. S7, it is apparent that it took much more time to achieve the adsorption equilibrium with higher initial concentration, implying that the adsorption occurred at first on the exterior surface of adsorbents, followed by the interior surface. It should be noted that magnetic activated carbon showed very fast adsorption rate, which can be described by the pseudo-second-order kinetic model with its kinetic rate (around $5 \times 10^{-4} \text{ g mg}^{-1} \text{min}^{-1}$).

Besides, to investigate the diffusion mechanism and elucidate rate-determining steps towards simulated adsorption, the intraparticle diffusion model was applied to obtain insight into the adsorption process and the equation was described as follows:

$$q_t = k_{\text{id}} t^{1/2} + c \quad (9)$$

where k_{id} ($\text{mg g}^{-1} \text{min}^{-0.5}$) is the intra-particle diffusion rate constant, and c (mg g^{-1}) is a constant related to boundary layer thickness.

If the intraparticle diffusion curve passes through the origin, then the intraparticle diffusion is the sole rate-limiting step. Or else, the adsorption process is controlled by some degree of

boundary layer.³³ As seen from Fig. 3 and Table S3, the curve was multi-linear and did not pass through the origin, implying that a rapid diffusion took place on the external surface of the adsorbent at first, followed by intraparticle diffusion of TCS, through which TCS molecules were migrated toward the sites where actual adsorption took place.³⁴

3.3.3 Effect of water matrix

The effect of solution pH on the TCS adsorption by activated carbon and magnetic activated carbon were carefully investigated in the pH value of 3-10. As shown in Fig. 4a, the adsorption capacity of TCS gradually decreased with an increase in pH at initial TCS concentration of 20 mg L⁻¹. It is partly attributed to electrostatic repulsion between deprotonated TCS and the negatively charged adsorbent surface.³ Moreover, the adsorption capacity of magnetic activated carbon was more sensitive to solution pH than that of activated carbon.

Real waters spiked with the initial TCS concentration of 20 mg L⁻¹ were used to further evaluate the effect of different matrix on the TCS adsorption. Clearly, the amounts of TCS adsorbed on activated carbon and magnetic activated carbon in pure water are relatively larger than that obtained in other water matrix (Fig. 4b). Generally, high pH and concentration of humic acid (HA) could inhibit the adsorption of TCS, as confirmed by Fig. 4a and Fig. S8.³⁵ Hence, it could be deduced that lower concentration of TOC as well as the lower solution pH of pure water would result in its higher adsorption capacity for TCS removal from aqueous solution (Table S4). Overall, magnetic activated carbon can act as an excellent adsorbent for TCS in real water matrix.

4. Conclusions

A novel magnetic activated carbon with developed porosity and excellent triclosan adsorption performance was synthesized from waste rice straw-derived hydrochar *via* activation and subsequent magnetization method. The increase in the activation temperature and the impregnation ratio promoted the development of porosity of activated carbon, which was closely associated to that of magnetic activated carbon. The spent magnetic activated carbon can be easily recovered by an external magnetic field. Compared to other known adsorbents, the as-prepared magnetic activated carbon possessed superior TCS adsorption capacity and fast adsorption rate. The present study indicated that the waste rice straw-derived hydrochar was a promising precursor for the synthesis of high-performance magnetic activated carbon in the removal of contaminants from real water matrix.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found on the online version.

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Figure captions:

Fig. 1 (a) X-ray powder diffraction (XRD) patterns of hydrochar (HC), activated carbon (AC) and magnetic activated carbon (MAC). X-ray photoelectron spectroscopy (XPS) spectra of magnetic activated carbon: (b) C1s high-resolution spectra, (c) O1s high-resolution spectra. (d) FT-IR spectra of hydrochar (HC), activated carbon (AC) and magnetic activated carbon (MAC).

Fig. 2 SEM images of (a) hydrochar (HC), (b) activated carbon (AC), (c) magnetic activated carbon (MAC), and TEM images of (d) hydrochar (HC) and (e) activated carbon (AC).

Fig. 3 Intraparticle diffusion kinetics for adsorption of TCS onto (a) activated carbon and (b) magnetic activated carbon at 298 K under different initial concentrations.

Fig. 4 (a) Effect of real water matrix on TCS adsorption onto activated carbon (AC) and magnetic activated carbon (MAC) at initial TCS concentration of 20 mg L^{-1} . (b) Effect of solution pH on TCS adsorption onto activated carbon (AC) and magnetic activated carbon (MAC) at initial TCS concentration of 20 mg L^{-1} .

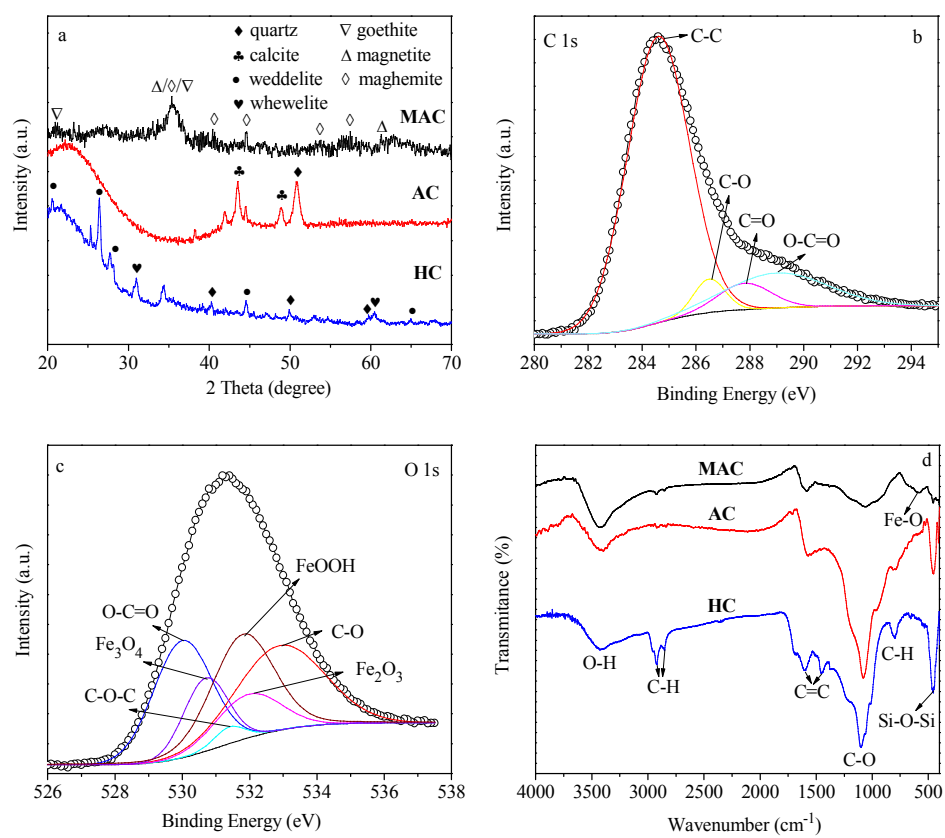


Fig. 1

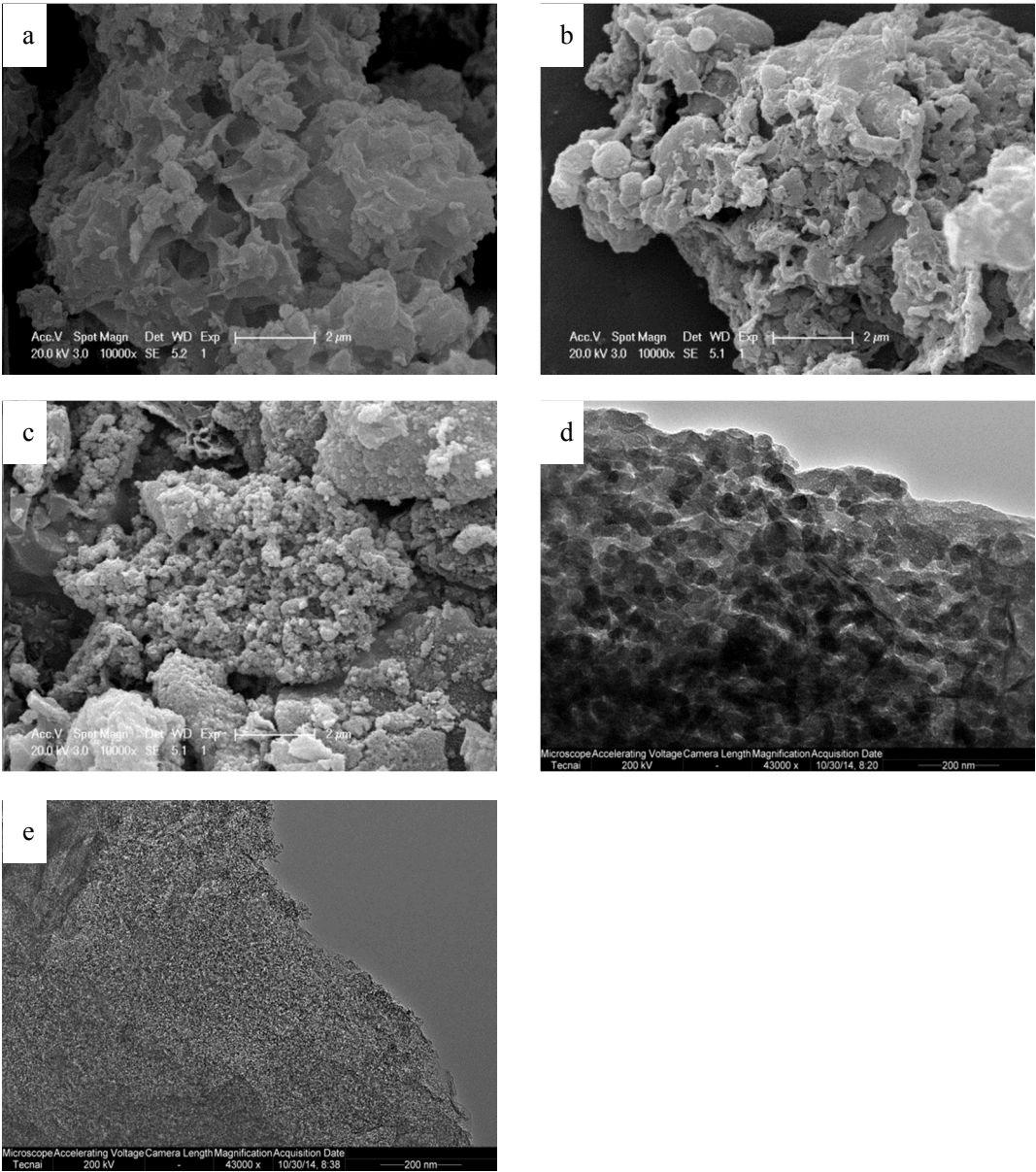


Fig. 2

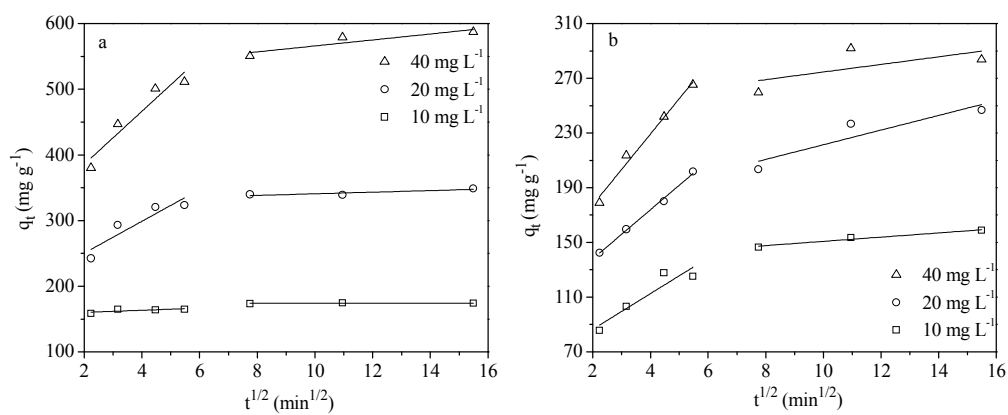


Fig. 3

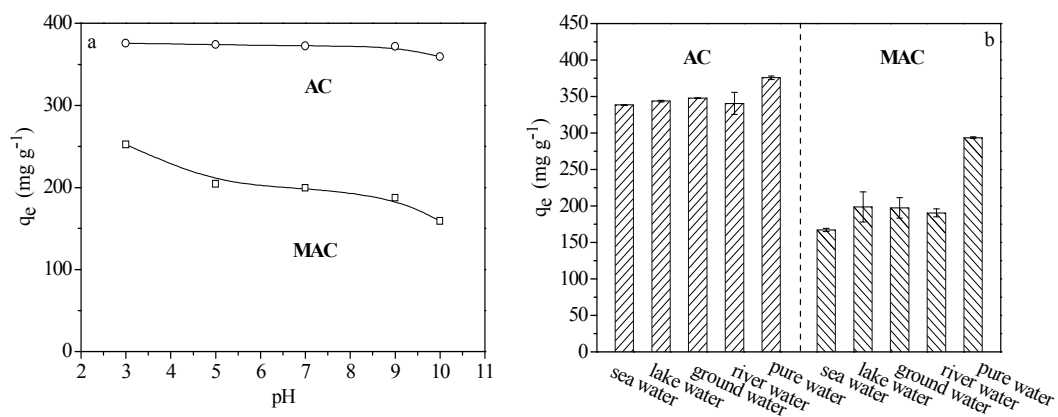


Fig. 4

Table 1 Textural properties of activated carbons prepared under different temperatures and impregnation ratios

Temperature (K)	Impregnation ratio ^a	Yield ^b (%)	S_{BET} ^c ($\text{m}^2 \text{g}^{-1}$)	S_{mic} ^d ($\text{m}^2 \text{g}^{-1}$)	$S_{\text{mic}}/S_{\text{BET}}$	V_{T} ^e ($\text{cm}^3 \text{g}^{-1}$)	V_{mic} ^f ($\text{cm}^3 \text{g}^{-1}$)	$V_{\text{mic}}/V_{\text{T}}$
773	2	57.0	308	256	0.83	0.26	0.13	0.50
873	2	49.9	506	437	0.86	0.41	0.22	0.54
973	2	30.8	697	595	0.85	0.49	0.29	0.59
1073	2	21.1	909	654	0.72	0.72	0.32	0.44
873	0.5	50.7	404	351	0.87	0.32	0.18	0.56
873	1	51.0	489	430	0.88	0.38	0.22	0.58
873	4	45.3	549	474	0.86	0.42	0.24	0.57

^a The weight ratio of K_2CO_3 to hydrochar. ^b The weight ratio of activated carbon to hydrochar. ^c Measured using N_2 adsorption with the Brunauer-Emmett-Teller (BET) method. ^d Micropore surface area calculated using the t -plot method. ^e Total pore volume determined at $P/P_0=0.99$. ^f Micropore volume calculated using the t -plot method.

Table 2 Textural properties for hydrochar (HC), activated carbon (AC) and magnetic activated carbon (MAC) samples

Sample	S_{BET}^a ($\text{m}^2 \text{g}^{-1}$)	S_{mic}^b ($\text{m}^2 \text{g}^{-1}$)	$S_{\text{mic}}/S_{\text{BET}}$	V_{T}^c ($\text{cm}^3 \text{g}^{-1}$)	V_{mic}^d ($\text{cm}^3 \text{g}^{-1}$)	$V_{\text{mic}}/V_{\text{T}}$
HC	6.22	-	0	0.06	-	0
AC	1334	1010	0.76	1.07	0.50	0.47
MAC	674	484	0.72	0.72	0.24	0.33

^a Measured using N₂ adsorption with the Brunauer-Emmett-Teller (BET) method. ^b Micropore surface area calculated using the *t*-plot method. ^c Total pore volume determined at *P*/*P*₀=0.99. ^d Micropore volume calculated using the *t*-plot method.

Table 3 Adsorption equilibrium constants obtained from Langmuir and Freundlich isotherms in the adsorption of TCS onto activated carbon (AC) and magnetic activated carbon (MAC) at 298K (q_m : mg g⁻¹, K_L : L mg⁻¹, K_F : mg^(1-1/n) g⁻¹ L^{1/n})

Sample	q_m	Langmuir			Freundlich		
		K_L	R_L	R^2	K_F	n	R^2
AC	714	0.52	0.04	0.97	232	2.25	0.64
MAC	303	0.89	0.02	0.99	150	4.68	0.91

Table 4 Kinetic parameters obtained from kinetic models for the adsorption of TCS onto activated carbon (AC) and magnetic activated carbon (MAC) at 298 K (C_0 : mg L⁻¹, $q_{e,exp}$: mg g⁻¹, $q_{e,cal}$: mg g⁻¹, k_1 :min⁻¹, k_2 : g mg⁻¹ min⁻¹, a : mg g⁻¹ min⁻¹, b : g mg⁻¹)

Sample	Pseudo-first-order					Pseudo-second-order			Elovich		
	C_0	$q_{e,exp}$	$q_{e,cal}$	k_1	R^2	$q_{e,cal}$	k_2	R^2	a	b	R^2
AC	10	174	8.94	0.014	0.52	175	0.0066	0.99	1.8×10^{16}	0.24	0.87
	20	349	67.7	0.023	0.93	357	0.0012	0.99	3.1×10^5	0.04	0.81
	40	587	167	0.023	0.99	588	0.0004	0.99	2.3×10^4	0.02	0.94
MAC	10	159	63.8	0.022	0.99	161	0.0010	0.99	4.6×10^2	0.05	0.95
	20	247	120	0.023	0.98	250	0.0005	0.99	9.7×10^2	0.04	0.98
	40	292	44.9	0.017	0.26	286	0.0010	0.99	6.8×10^3	0.04	0.88