Adsorption of creatinine on active carbons with nitric acid hydrothermal modification

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Abstract

The adsorption of creatinine on active carbons was studied. Original active carbon (AC) and AC samples modified by nitric acid hydrothermal modification were assessed for their ability to adsorb creatinine. The pore structure and surface properties of the AC samples were characterized by N₂ adsorption, temperature programmed desorption (TPD), Fourier Transform Infrared spectroscopy (FTIR), and X-ray photoelectron spectrometer (XPS). It indicated that 4M HNO₃ hydrothermal modification with 180 °C was an efficient method in improvement of the creatinine adsorption. The improved adsorption capacity can be attributed mainly to an increase in the acidic oxygen-containing functional groups. The adsorption of creatinine over AC may involve an interaction with the acidic oxygen-containing groups on AC. Langmuir and Freundlich adsorption models were applied to describe the experimental isotherm and isotherm constants. Equilibrium data fitted very well to the Freundlich model in the entire saturation range (3.58-59.08 mg L⁻¹). The maximum adsorption capacities of AC modified with 180 °C is 62.5 mg g⁻¹ according to the Langmuir model. Pseudo first-order and second-order kinetic models were used to describe the kinetic data and the rate constants were evaluated. The experimental data fitted well to the second-order kinetic model, which indicates that the chemical adsorption was the rate-limiting step, instead of mass transfer.

Keyword: Creatinine; Active carbon; Nitric acid; Hydrothermal; Adsorption

1.0 Introduction

Creatinine (2-amino-1-methyl-5H-imidazol-4-one, $C_4H_7N_3O$) is a typical uremic toxin in the human metabolism products. The accumulation of creatinine in the blood causes a series of toxic symptoms such as diabetic nephropathy, eclampsia, glomerulonephritis, muscular dystrophy, and preeclampsia, meanwhile which also reduces the kidney function and accelerates the renal decline [1].

Creatinine is commonly removed by haemodialysis. However, creatinine cannot be effectively removed by a single haemodialysis process. Haemoperfusion, the direct contact of the patients' blood with sorbents, can efficiently remove toxins without introducing any other substances into the blood [2]. Porous materials such as active carbon and polymeric resin are mainly used in haemoperfusion [3] to adsorb the creatinine. To date, porous materials like active carbon [4], zeolites [5-7], carbon nanotubes [8], molecularly imprinted polymers [9-11], and metal-organic frameworks [12] for artificial kidney application of creatinine adsorption have been investigated.

Among those adsorbents, activated carbon (AC) has a long record as a cheap sorbent in blood purification in the case of intoxications, acute and chronic renal failure as well as liver failure [13-15]. Moreover, carbon materials have chemically inert surface and excellent biocompatibility, they are more powerful sorbents than their inorganic or organic counterparts because they do not require special coatings [16].

On the other hand, creatinine not only exists in serum, but also in the alimentary canal (stomach and intestine) [17]. Active carbon can be used as oral sorbents to reduce the creatinine concentration in serum. Creatinine and other waste nitrogenous waste products (urea, etc) which diffuse into the gastrointestinal tract from the blood are bound to active carbon and excreted in the

feces, creating a concentration gradient for continued diffusion, giving place to a process this intestinal dialysis. Therefore, active carbon can adsorb the creatinine, uric acid and other toxins in gastrointestinal tract quickly, lightening the burden of kidney excreting toxins [18, 19].

Both porous structure and surface chemistry of ACs may play an important role in determining their adsorption performance. Since the performance of AC in most applications is influenced by its surface chemistry, the modification of its properties has been the target of a variety of treatments. Nitric acid has been used to introduce carbon-oxygen surface groups in AC to increase the adsorption capacity for phenol [20] and sulfur compounds [21] in aqueous phase. Nitric acid modified AC samples were also used for vapor adsorption [22], which decreased the butanol adsorption capacity due to the increased oxygen-containing functional groups on the adsorbents' surface [23]. It indicates that different adsorbates may have different interaction with the oxidized AC samples. To improve the adsorption performance of AC for removing creatinine, hydrothermal modification of the commercial AC was conducted in the present study by using 4 M HNO₃ at 120 °C, 150 °C and 180 °C, respectively. To our knowledge, similar research has not been reported so far.

2.0 Materials and methods

2.1 Materials

HNO₃ and creatinine (Assay Percent Range: 99+%, C₄H₇N₃O) were purchased from Thermo Fisher Scientific Inc. All of these chemicals were analytical grade. Commercial AC was purchased from Thermo Fisher Scientific Inc. Different kinds of modified AC were obtained by reaction between commercial AC and 4M HNO₃ at different temperatures.

2.2 Methods

2.2.1 Modification of AC

The commercial AC was washed by boiling water with a Soxhlet extractor for 2 hours. The wet AC was dried at 105 °C for 24 hours. 3 g of the dried AC was reacted with 40 ml 4M HNO₃ in a sealed PTFE reactor (50ml) at 120, 150, and 180 °C for 1 hour respectively. These samples are denoted as 120-AC, 150-AC, and 180-AC. After reaction, the reactant was cooled and filtered, and washed with deionized water under vacuum filtration until the pH value of the permeate was ~7. Finally, the washed AC was dried in a vacuum oven at 105 °C overnight.

2.2.2 Chemical and textural characterization for absorbents

The characterization of the porous texture of the ACs was carried out by the analysis of the adsorption isotherm adsorption of N₂ using an ASAP 2020 Micropore Analyzer. The total pore volume was determined at relative pressure 0.995 P₀, and the specific surface area was calculated from the BET method. The micropore and mesopore volume and the pore size distribution were determined by the density functional theory (DFT) for samples based on the N₂ isotherm adsorption data.

Temperature-programmed desorption (TPD) was performed using a Micrometrics Autochem II Chemisorption Analyzer to investigate the oxygen content of these four AC samples. The carbon sample (0.05 g) was placed in a U-shaped quartz tube inside an electrical furnace and heated at 10 °C/min up to 1000 °C using a constant flow rate of helium (the flow rate of the vapor, carrier, and reference were set at 0, 60, and 60 cm³/min respectively). The thermal conductivity detector (TCD) signals were monitored during the thermal analysis, and the corresponding TCD spectra was obtained.

In order to analyze the functional groups on the surface, FTIR analysis of AC samples were carried out by using UV-3600 spectrophotometer within the range of 600-4000 cm^{-1} . The AC samples were dried in an oven at 110 °C for overnight before the FTIR analysis. XPS analysis was carried out using Kratos Axis Ultra X-ray photoelectron spectrometer with concentric hemispherical electron energy analyzers combined with the established delay-line detector (DLD). The incident radiation monochromatic Al K α X-ray (1486.6 eV) at 150W (accelerating voltage 15kV, emission current 10mA) was projected 45° to the sample surface and the photoelectron data was collected at takeoff angle of $\theta = 90^\circ$. The absolute energy scale was calibrated to Cu 2p $_{3/2}$ peak binding energy at 932.6 eV using sputter etched 99.9999% pure copper foil. The base pressure in the analysis chamber was maintained at 1.0×10^{-9} torr. Low energy electrons were used for charge compensation to neutralize the sample. Carbon powders were pressed onto 99.999% pure Indium foil for analysis. Survey scans were taken at pass energy of 160 eV, and carried out over 1200 eV ~-5 eV binding energy range with 1.0 eV steps and a dwell time of 200 ms. High resolution scans of C 1s, O 1s, and N 1s were taken at pass energy of 20 eV with 0.1 eV steps and a dwell time of 1000ms. The spectra analyses were carried out using CasaXPS version 2.3.17dev6.4k. Shirley type background was routinely used to account for inelastically scattered electrons that contribute to the broad background. Transmission corrected RFS/Kratos library relative sensitivity factors (RSFs) was used for elemental quantification. The spectra were calibrated using adventitious carbon C 1s peak at 285.0 eV.

2.2.3 Quantification of creatinine

To determine the amount of creatinine adsorbed by the adsorbents, a standard curve was used to calculate the creatinine amount in the solution. Creatinine was dissolved in distilled water, and creatinine solutions with different concentrations (2, 4, 8, 10, 20, 40, 60, 80, 100, 120, 140,

and 160 mg/L) were prepared. The ultraviolet (UV) region of 120 mg/L creatinine solution is scanned from 200 to 400 nm by a Shimadzu UV 2450 spectrophotometer (Tokyo, Japan). As is shown in Fig. S1, the wavelength of maximum absorbance is 230 nm. Therefore, the absorbance of the solution was measured at 230 nm. The standard curve was plotted according to the concentration and absorbance, which is shown in Fig. S2. Regression of the standard absorbance with concentration typically resulted in an $R^2 \geq 0.99$.

2.2.4 Batch equilibrium

The creatinine was dissolved in deionized water to the required concentration. In experiments of equilibrium adsorption isotherm, AC sample (50 mg) of and creatinine solution (20 mL) were placed in a 100 mL Erlenmeyer flask and shaken for 2 h by an incubator at the constant temperature of 37 °C. Each used a range of initial creatinine concentration was 40, 60, 80, 100, 120, 140 and 160 mg/L at pH 7. The AC sample was removed via a Millipore membrane filter (0.20 µm) and the permeate was measured in the UV Spectrometer at 230 nm to determine the concentration of creatinine in the solution. Every value reported contained at least three separate measurements, and standard deviation was less than 5%. The amount of adsorption at equilibrium q_e (mg/g) was calculated as follows:

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

Where C_0 and C_e (mg/L) are the initial and equilibrium creatinine concentration respectively. V (L) is the volume of the solution and W (g) is the weight of AC used.

2.2.5 Batch kinetic

In experiments of batch kinetic adsorption, 50mg of different AC samples were weighed and both the samples and the 160mg/L creatinine solution were heated to 37 °C in an incubator. The 160mg/L creatinine solution was mixed in the incubator constantly at 100 rpm. Once the samples warmed, 20mL of creatinine solution were added to each sample in Erlenmeyer flasks and samples were removed at 1, 3, 5, 15, 30, 60 or 120min via membrane filters. The creatinine concentration was determined as above-mentioned measuring method.

2.2.5 Data analysis

The widely used Langmuir isotherm has found successful application in many real adsorption processes and is expressed as:

$$q_e = \frac{QbC_e}{1+bC_e} \quad (2)$$

which can be rearranged to obtain a linear form

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (3)$$

where Q (mg g⁻¹) refers to the monolayer adsorption capacity, q_e is amount of adsorption at equilibrium, C_e (mg L⁻¹) is the creatinine concentration at equilibrium and b is the Langmuir constant.

The Freundlich isotherm, used for isothermal adsorption, is a special case for heterogeneous surface energy in which the energy term in the Langmuir equation varies as a function of surface coverage strictly due to variation of the adsorption [24]. The Freundlich equation is given as:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (4)$$

where C_e is the equilibrium concentration of adsorbate (mg L^{-1}), q_e is the amount of the creatinine adsorbed by the adsorbents at equilibrium (mg g^{-1}), k_f ($(\text{mg/g}) (\text{dm}^3/\text{mg})^{1/n}$) and n are indicators of adsorption capacity and adsorption intensity, respectively. k_f and n can be determined from the linear plot of $\ln q_e$ versus $\ln C_e$.

In order to investigate the mechanism of adsorption, the pseudo first-order and second-order equations were used to test the experimental data. The first-order rate expression of Lagergren [13] is given as:

$$\log(q_e - q) = \log q_e - \frac{k_1 t}{2.303} \quad (5)$$

where q_e and q are the amounts of urea nitrogen adsorbed onto adsorbent at equilibrium and at time t , respectively, and k_1 (min^{-1}) is the rate constant of first-order adsorption. The second-order kinetic model is expressed as:

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

Where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of second-order adsorption.

3.0 Results and discussion

3.1. Physicochemical properties of active carbons

3.1.1 Pore structure characterization

Nitrogen adsorption-desorption isotherms of unmodified AC, 120-AC, 150-AC and 180-AC are shown in Fig. 1A. All nitrogen adsorption isotherms are of type II according to the classification by Brunauer et al [25]. The N_2 adsorption capacity on the ACs increased in the order of $120\text{-AC} < 150\text{-AC} < 180\text{-AC} < \text{AC}$. A hysteresis loop was observed at the relative high pressure

for each AC sample, indicating the presence of mesopores, which can also be found from the density functional theory (DFT) mesopores size distribution of the ACs, as is shown in Fig. 1B. It indicates that the pore volumes for micropores (smaller than 2nm) and mesopores (from 2nm to 50 nm) were slightly decreased for 120-AC and 150-AC samples. Fig. 1C shows the cumulative pore volumes for the AC samples, the curves for 120-AC and 150-AC, 180-AC and AC are almost overlapped respectively, which indicates their pore size distributions are almost the same for each pair. However, compared with the untreated AC, the total pore volume decreased from 0.76 to 0.70, 0.70, and 0.72 $\text{cm}^3 \text{g}^{-1}$ for 120-AC, 150-AC and 180-AC respectively, which is shown in Table 1. The pores less than 50 nm (micropore volume plus mesopore volume) was decreased from 0.45 to 0.41 $\text{cm}^3 \text{g}^{-1}$ for both 120-AC and 150-AC, while there is no change for AC treated with 180 °C. With the total pore volume decreased after the modification, the BET surface areas for the AC-120, AC-150, and AC-180 decreased from 909 (unmodified AC) to 847, 869, 883 $\text{m}^2 \text{g}^{-1}$, respectively (Table 1).

The nitric acid hydrothermal treatment decreased the micropores volume for 0.03, 0.02 and 0.01 $\text{m}^2 \text{g}^{-1}$ at 120, 150, and 180 °C, respectively, which can be attributed to partial destruction of the porous structure of the original sample due to the erosion of micropore walls [20, 26]. The mesopore volume decreased from 0.16 to 0.15 $\text{cm}^3 \text{g}^{-1}$ with reaction temperature increased from 120 to 150 °C, which caused mesopores partially transferred into micropores [23]. It is likely due to the partial destruction of the pore structure and the introduced oxygen-containing functional groups at the active sites at the entrance of the mesopores [20, 26]. This resulted in the average pore diameter of the 120-AC and 150-AC decreased from 3.34 (unmodified AC) into 3.31 and 3.22 nm, respectively (Table 1).

On the contrary, compared with 150-AC the mesopore volume slightly increased ($0.01 \text{ cm}^3 \text{ g}^{-1}$) for 180-AC. Higher temperature enhanced oxidation reaction much more greatly, causing more robust oxidation and etching of the carbon matrix of AC. It generated some new micropores, meanwhile, some of the micropores were widened into mesopores. Therefore, the average pore diameter of 180-AC (3.26 nm) was slightly larger than that of 150-AC (3.22 nm), as is shown in Table 1.

3.2.2 Oxygen-containing functional groups on ACs

Temperature-programmed desorption (TPD) was employed to investigate the functional groups generated by HNO_3 modification [22]. The carrier gas helium and the detected gases (CO , O_2 and CO_2) have different thermal conductivities. TCD signals from the evolved gases were recorded and the areas under the peak were proportional to the amount of gases produced. Therefore, the TPD profile roughly indicates the amount of oxygen-containing functional groups.

Fig. 1D displays the TPD spectra arising from oxygenated groups released as CO and CO_2 from the surface of ACs. The TPD profile measured for the untreated AC was also included. The quantity of oxygenated groups released during treatment was directly related to the temperature used to treat AC. Generally, carboxylic functional groups decompose and release H_2O at lower temperatures (100°C to 400°C), while anhydride and lactone groups decompose at higher temperatures (427°C) [27-29]. In this study, the peaks formed between 400 - 1000°C were assumed to be CO_2 and CO [30], and the CO was possibly derived from the decomposition of phenols, ethers and carbonyls/quinones [31-33]. The order of oxygen-containing functional group's amount was $\text{AC-180} > \text{AC-150} > \text{AC-120} > \text{unmodified AC}$ according to the TPD profiles. The level of oxygen functional groups that are created on the AC surface is dependent on the treatment conditions, including nitric acid concentration, temperature and amount of carbon loaded [34]. It

indicates that higher temperature can generate more oxygen-containing functional groups due to more vigorous oxidation with higher temperature.

As is shown in Fig. S3, there are two major characteristic peaks in the range of 1800-1400 cm^{-1} , which are mainly absorption bands of C=O and aromatic ring. The peak centered at 1722 cm^{-1} can be contribution from the stretching vibrations of carboxyl groups (C=O) on the edges of layer planes or from conjugated groups in the lactone groups. The peak at 1563 cm^{-1} can be assigned to asymmetric COO^- vibration. The peak around 1158 cm^{-1} can be ascribed to the both C-O stretching and O-H bending modes in phenolic and carboxylic groups. Compared with the unmodified AC, it was observed that the 180-AC had higher absorption intensity at 1722, 1563 and 1158 cm^{-1} , indicating an increase in carboxyl, lactone, and hydroxyl groups [21]. After TPD, these absorptions decreased significantly. It means that high temperature decomposed those oxygen-containing functional groups.

It was found that the HNO_3 hydrothermal oxidation would change the total surface area and pore distribution to some extent as discussed above, but the surface morphology of ACs were almost the same, as is shown in Fig. S4. However, after HNO_3 treatment, oxygen content in the AC increased significantly, which has been verified by SEM-EDS (Table S1). The order of total oxygen content was unmodified AC (4.39, wt. %) < 120-AC (7.67, wt. %) < 150-AC (8.50, wt. %) < 180-AC (11.83, wt. %).

The kinds and amounts of surface functional groups on unmodified AC and 180-AC were more quantitatively determined by the XPS method. Fig. 2 Shows the C 1s and O 1s XPS spectra of unmodified AC and 180-AC. After baseline correction using Shirley's method, the C 1s peak of these two samples can be deconvoluted into five peaks centered at 284.6, 286.0, 287.3, 288.9, and 290.3 eV, which are ascribed to the graphitic C=C bond, -C-O, -C=O, O-C=O, and CO_3 groups,

respectively [35-37]. The O 1s peak of each sample contains contributions from two Gaussian deconvoluted peaks centered at 532.0 and 534.0 eV, which are attributed to =O and -O- species, respectively [38]. Table 2 shows the molar ratio distribution of surface functional groups on unmodified AC and 180-AC from a comparison of each deconvoluted peak. By contrast, oxidation at 180 °C increased C-O group amount (199.8% higher than the unmodified AC) accompanied by simultaneous increase in C=O, O-C=O (e.g., -COOH). The C1s spectra (Table 2) displayed higher carbonyl (or quinone) and carboxylic (or ester or lactone) groups contents in 180-AC (2.81% of C=O group; 2.81% of O-C=O groups) compared to the unmodified AC sample (1.96% of C=O, and 2.25% of O-C=O). However, the nitric acid modification slightly reduced the concentration of CO₃ from 3.10% to 2.90%, probably due to the removal of carbonate existing in unmodified AC during the oxidation treatment. The O1s spectra shows the intensity of the oxygen components in form of -O and =O. As is shown in Fig. 2, the intensity of the 180-AC was higher than that of unmodified AC. The oxygen content of 180-AC was 4.17% for =O and 5.67% for -O-, which was significantly higher than unmodified AC (1.88% for =O and 2.15% for -O-).

3.2 Equilibrium adsorption

Fig. 3A shows the equilibrium adsorption of creatinine onto the four AC samples with different concentrations. With the increasing initial concentration of creatinine, the equilibrium adsorption capacity for creatinine increased gradually until the equilibrium condition is reached [39], showing the favourable adsorption of creatinine on AC samples at higher concentrations. It indicates that the AC-180 has the highest adsorption capacity among these four adsorbents. To compare the saturation adsorption capacity, we also investigated the saturation adsorption for ACs. As is shown in Fig. 3B, the creatinine adsorbed by the ACs was increasing until the creatinine solution volume increased to 80 ml. The 180-AC got the highest amount of creatinine adsorption

at equilibrium (64.5 mg g^{-1}), which is 0.29 times more than the unmodified AC (50.0 mg g^{-1}). It indicates the modification greatly enhanced the creatinine adsorption capacity.

3.2.1 Langmuir isotherm

A linearized plot of C_e/q_e versus q_e was obtained from the model shown in Fig. S5. Q and b is computed from the slopes and intercepts of different straight lines representing different AC samples. Table 3 lists the calculated results. It indicates that the computed maximum monolayer capacity Q of creatinine onto unmodified AC, 120-AC, 150-AC and 180-AC are 55.6, 71.4, 62.5 and 62.5 mg g^{-1} , respectively. However, the fits are not quite well for the AC samples under the creatinine concentration ranges studied, and correlation coefficients of unmodified AC, 120-AC, 150-AC and 180-AC are 0.9422, 0.9070, 0.9335 and 0.9830, respectively. It indicates that the adsorption of creatinine was not typical monolayer [40].

3.2.2. Freundlich isotherm

The values of the Freundlich adsorption isotherm constant n were 2.02, 1.63, 1.95 and 2.12 for the unmodified AC, 120-AC, 150-AC and 180-AC, respectively (Table 3). All the values were within 1-10, indicating that the adsorption for creatinine by these adsorbents were favorable [41, 42]. As a result, the Freundlich adsorption model, which was considered to be the uneven adsorption mainly via monolayer chemical adsorption and a small amount of physical adsorption on the surface of the adsorbent, could be applied in the adsorption process for creatinine.

3.3 Kinetics of adsorption

Fig. 3D, F and H show the adsorption kinetics of creatinine onto AC samples at initial concentrations 160, 120 and 80 mg L^{-1} at 37°C . It shows that adsorption was quick in the first 15 min and the equilibrium was reached within 2 h for 160 mg L^{-1} . While it takes 90 and 60 min to

reach the equilibrium at initial creatinine concentrations 120 and 80 mg L⁻¹, respectively. At initial concentration 160 mg L⁻¹, the adsorption capacity q_e at equilibrium is 40.3, 42.6, 42.8 and 46.5 mg g⁻¹ for unmodified AC, 120-AC, 150-AC and 180-AC, respectively. It indicates that the adsorption capacity increased after nitric acid hydrothermal modification [24], which might due to the oxygen-containing functional groups such as strong carboxylic acids (-COOH), phenols (-OH) and carbonyls/quinones (=O) generated by oxidation [34]. Similar to the trends for initial concentration at 120 and 80 mg L⁻¹, AC modified by 4 M nitric acid with 180 °C obtained the fastest adsorption speed and highest adsorption capacity for creatinine.

3.4 Rate constant

As is shown in Fig. S6, log ($q_e - q$) versus t shows a poor agreement of experimental data with a first-order kinetic model with different initial creatinine concentrations (80, 120 and 160 mg L⁻¹). This suggests the adsorption of creatinine onto AC sample is not a first-order reaction.

It can be seen from Fig. 3E, G and I that the plots of t/q versus t show a linear relationship for each AC sample. The slopes and intercepts of plots of t/q versus t were used to calculate the second-order rate constant k_2 and q_e . The straight lines in plot of t/q versus t (Fig. 3E, G and I) show a good agreement of experimental data with second-order kinetic model for different AC samples with different initial creatinine concentrations. Tables 4-6 list the calculated results obtained from the second-order kinetic model. The correlation coefficients for the second-order kinetic model, which are also presented in Tables 4-6, are higher than 0.99 for all the cases. These suggest that the adsorption of creatinine onto AC samples follows the second-order kinetic model and chemical adsorption might be the rate-limiting step [40]. Table 7 compares the adsorption capacity of different types of adsorbents used for removal of creatinine [4, 5, 8]. It can be seen the AC-180 has higher adsorption ability than that of most adsorbents reported in other literatures.

Creatinine is one of the uraemic toxins in the blood, which is low molecular weight toxin. Some other middle molecular toxins could also be adsorbed by the active carbon during the adsorption. By comparing the adsorption capacities for the adsorption of creatinine onto various adsorbents such as carbon nanotube, zeolite, poly(ether sulfone)/activated carbon, it indicates that the surface functioned active carbon obtained by nitric acid hydrothermal modification get the highest adsorption capacity. Although the adsorption by AC is non-selective, it can potentially be employed to clinic application due to low cost without introducing any other substances into the blood [8]. Meanwhile, carbon filter and ion-exchange resin have been used to regenerate the adsorbent after dialysis [43]. Therefore, we are trying to develop new surface functioned AC adsorbents, and looking forward to collaborate with Sanford Healthcare to develop some real tests with clinic dialysis liquid samples, and consider competition from other biomolecules. In addition, one crucial factor impacting adsorption of creatinine by AC is the depletion of adsorption sites [44], competition and pore blockage during active carbon adsorption hampers the adsorption efficiency [45]. More work is needed to better understand how to optimize the adsorption of creatinine and other toxins in the blood.

3.5 Mechanism of creatinine adsorption onto nitric acid modified AC

There are two possible tautomers of creatinine, the imine 1 and amine 2 forms [46], as is shown in Fig. 3Ja. The amine 2 predominates in solution [47]. After HNO_3 oxidation, some carboxylic acid groups were generated by the treatment as discussed above. Therefore, the amine (creatinine) and carboxylic acid reacted and formed covalent bond (Fig. 3Jb), the water produced and an amide was formed. This reaction enhanced the creatinine adsorption quantity by using the HNO_3 -modified ACs as sorbents. A hydrogen ion can break away from the phenolic group on the surface of the modified AC. The creatinine molecule combined with the hydrogen ion and was

protonated [6, 48], which would be “adsorbed” by the negatively charged site from the previous phenolic group. This mechanism is shown in Fig. 3Jc, which indicates the pyridine-N-oxide structure was formed. The N1 spectra of AC-180 and creatinine-adsorbed AC-180 verified these formations.

Fig. 4 shows the deconvoluted N 1s spectra of 180-AC and creatinine adsorbed 180-AC. The N 1s spectra of these samples can be deconvoluted into different peaks centered at 399.7 (N1 component), 400.6 (N2 component), 401.4 (N3 component), 403.0 (N4 component), and 406.5 eV (N5 component). According to the literature review, pyridinic-type nitrogen gives rise to a peak about 398.6 eV [49], the binding energy of nitrogen in amides can be at about 399.7 eV [50, 51]. Nitrogen in pyrrole and lactam groups was found to be at 400.3 [52] and 400.1 eV [53], respectively. The contribution at 401.5 eV has been assigned to various forms of quaternary nitrogen atoms [54]. Furthermore, the peak at 402-405 eV was identified to arise from pyridine-N-oxide[55]. The higher binding energy around 406.5 eV can be attributed to N 1s of -NO₂ [56]. Based on these literature reports, the N1 peak can be assigned to amide, and N2 peak to lactam and pyrrole groups. The N3 component can be assigned to highly coordinated nitrogen atoms bound to three C atoms in the bulk of a graphene layer and the N4 peak to the pyridine-N-oxide, which gives a peak above 402.0 eV [57]. Finally, the N5 peak can be NO₂ group on the modified AC. As is shown in Table 8, the total nitrogen concentration was increased from 0.74 to 2.58 % after adsorption. To assess the amount of different types of N-species, the relative percentage of different N-groups was calculated based on the deconvoluted N 1s spectra (Table 8). AC-180 shows two peaks: a low binding energy component (N3) centered at 401.4 eV and a higher binding energy component (N5) centered at 406.5 eV. In case of creatinine adsorbed 180-AC, three other peaks (N1, N2 and N4) appeared. It indicates that nitrogen component N1 increased 0.91%, which

agrees with the amide formed in Fig. 3Jb. The N2 species and the increased amount of N3 species of creatinine adsorbed 180-AC, which may come from the creatinine itself. N4-type-nitrogen species (0.15%) was from the pyridine-N-oxide formed according to the combination shown in Fig. 3Jc. While the N5 component remained the same after the adsorption since there was no reaction to the $-\text{NO}_2$ group during the adsorption. The carboxyl and phenolic groups generated by HNO_3 oxidation combined with the creatinine molecules, therefore, the creatinine adsorption capacity increased after HNO_3 treatment.

4.0 Conclusions

After 4M HNO_3 hydrothermal modification at 180 °C, the total surface oxygen content was increased 2.69 times. Although the BET surface area was decreased by 26 $\text{m}^2 \text{g}^{-1}$, the creatinine saturation adsorption capacity in 180-AC was 29% higher than the unmodified AC. The improvement of the adsorptive performance by the HNO_3 oxidation modification is dominantly through an increase of the oxygen-containing functional groups on the AC surface. N 1s XPS results indicate carboxyl and phenolic groups generated by HNO_3 oxidation can potentially “adsorb” (reacted with) creatinine. Freundlich model and second-order kinetic model fitted very well to the equilibrium isotherm and the dynamical behavior for the adsorption of creatinine onto the HNO_3 -modified ACs. These suggested that the rate-limiting step might be chemical adsorption but not mass transfer.

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Figure captions

Fig. 1. (A) N₂ adsorption–desorption isotherms of ACs; (B) DFT pore size distribution curves of the absorbents; (C) Cumulative pore volumes of the absorbents; (D) TPD profiles of ACs.

Fig. 2. (A) C 1s and (B) O 1s XPS spectra of (a) unmodified AC, (b) 180-AC.

Fig. 3. (A) Equilibrium adsorptions of creatinine onto AC samples; (B) Saturation adsorption capacities of creatinine at 160 mg L⁻¹; (C) Freundlich plots for AC samples; Adsorption kinetics of different initial creatinine concentrations: (D) 160 mg L⁻¹; (F) 120 mg L⁻¹; (H) 80 mg L⁻¹. Plots of pseudo second-order model of different initial creatinine concentrations: (E) 160 mg L⁻¹; (G) 120 mg L⁻¹; (I) 80 mg L⁻¹. (J) Tautomers of creatinine and possible reactions between HNO₃-modified AC and creatinine.

Fig. 4. N 1s XPS spectra of (a) 180-AC, (b) creatinine adsorbed 180-AC.

A

B

C

D

Fig. 1. (A) N₂ adsorption–desorption isotherms of ACs; (B) DFT pore size distribution curves of the absorbents; (C) Cumulative pore volumes of the absorbents; (D) TPD profiles of ACs.

A

B

Fig. 2. (A) C 1s and (B) O 1s XPS spectra of (a) unmodified AC, (b) 180-AC.

A

B

C

D

E

F

G

H

I

J

Fig. 3. (A) Equilibrium adsorptions of creatinine onto AC samples; (B) Saturation adsorption capacities of creatinine at 160 mg L⁻¹; (C) Freundlich plots for AC samples. Adsorption kinetics of different initial creatinine concentrations: (D) 160 mg L⁻¹; (F) 120 mg L⁻¹; (H) 80 mg L⁻¹. Plots of pseudo second-order model of different initial creatinine concentrations: (E) 160 mg L⁻¹; (G) 120 mg L⁻¹; (I) 80 mg L⁻¹. (J) Tautomers of creatinine and possible reactions between HNO₃-modified AC and creatinine.

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Table caption

Table 1 Surface area and pore structure parameters of the absorbents.

Table 2. Surface functional group molar ratio distributions obtained by XPS measurement.

Table 3. The parameters of Langmuir adsorption isotherm model and the Freundlich adsorption isotherm model.

Table 4. The parameters of second-order adsorption rate constants and calculated q_e for different AC samples at initial concentration (160 mg/L).

Table 5. The parameters of second-order adsorption rate constants and calculated q_e for different AC samples at initial concentration (120 mg/L).

Table 6. The parameters of second-order adsorption rate constants and calculated q_e for different AC samples at initial concentration (80 mg/L).

Table 7. Adsorption capacities for the adsorption of creatinine onto various adsorbents.

Table 8. Surface nitrogen composition of AC-180 and creatinine adsorbed 180-AC derived from XPS.

Table 1 Surface area and pore structure parameters of the absorbents.

Sample #	$S_{\text{BET}}^{\text{a}}$ $\text{m}^2 \text{g}^{-1}$	$V_{\text{Total}}^{\text{b}}$ $\text{cm}^3 \text{g}^{-1}$	$V_{\text{Micro}}^{\text{c}}$ $\text{cm}^3 \text{g}^{-1}$	$V_{\text{Meso}}^{\text{d}}$ $\text{cm}^3 \text{g}^{-1}$	$D_{\text{Average}}^{\text{e}}$ nm
Unmodified AC	909	0.76	0.28	0.17	3.34
120-AC	847	0.70	0.25	0.16	3.31
150-AC	869	0.70	0.26	0.15	3.22
180-AC	883	0.72	0.27	0.18	3.26

^a BET (Brunauer-Emmett-Teller) surface area^b Total pore volume, measured at $P/P_0=0.995$ ^c Micropore volume, based on density functional theory (DFT)^d Mesopore volume, based on density functional theory (DFT)^e Average pore diameter of absorbents, calculated by $4V_{\text{Total}}/S_{\text{BET}}$ **Table 2.** Surface functional group molar ratio distributions obtained by XPS measurement.

Sample	C 1s					O 1s	
	C=C	C-O	C=O	O-C=O	CO ₃	=O	-O-
Unmodified AC	87.47	5.21	1.96	2.25	3.10	1.88	2.15
180-AC	81.06	10.41	2.81	2.81	2.90	4.17	5.67

Table 3. The parameters of Langmuir adsorption isotherm model and the Freundlich adsorption isotherm model.

Samples	Langmuir			Freundlich		
	R^2	$Q (\text{mg g}^{-1})$	$b (\text{L mg}^{-1})$	R^2	n	$k_f (\text{mg/g}) (\text{dm}^3/\text{mg})^{1/n}$
Unmodified AC	0.9422	55.6	0.0379	0.9936	2.02	5.18
120-AC	0.9070	71.4	0.0243	0.9870	1.63	3.59
150-AC	0.9335	62.5	0.0376	0.9919	1.95	5.41
180-AC	0.9830	62.5	0.0690	0.9977	2.12	8.09

Table 4. The parameters of second-order adsorption rate constants and calculated q_e for different AC samples at initial concentration (160 mg/L).

Samples	Second-order kinetic model		
	$k_2 (\text{g mg}^{-1} \text{min}^{-1})$	$q_{e,\text{cal}} (\text{mg g}^{-1})$	R^2
Unmodified AC	2.976E-2	40.0	0.9997
120-AC	1.707E-2	43.5	0.9990
150-AC	1.858E-2	41.7	0.9995
180-AC	2.940E-2	47.6	0.9990

Table 5. The parameters of second-order adsorption rate constants and calculated q_e for different AC samples at initial concentration (120 mg/L).

Samples	Second-order kinetic model		
	$k_2(\text{g mg}^{-1} \text{ min}^{-1})$	$q_{e,\text{cal}} (\text{mg g}^{-1})$	R^2
Unmodified AC	20.08	30.2	0.9999
120-AC	25.79	33.8	0.9999
150-AC	29.09	34.6	0.9999
180-AC	31.51	38.0	0.9999

Table 6. The parameters of second-order adsorption rate constants and calculated q_e for different AC samples at initial concentration (80 mg/L).

Samples	Second-order kinetic model		
	$k_2(\text{g mg}^{-1} \text{ min}^{-1})$	$q_{e,\text{cal}} (\text{mg g}^{-1})$	R^2
Unmodified AC	6.83	20.2	0.9999
120-AC	45.20	25.0	0.9994
150-AC	37.08	25.2	0.9997
180-AC	31.66	27.6	0.9998

Table 7. Adsorption capacities for the adsorption of creatinine onto various adsorbents.

Adsorbent	Adsorption capacity (mg g^{-1})	Reference
AC-180	64.5	This work
Poly(ether sulfone)/activated carbon	28.0	[4]
Zeolite	37.0	[5]
Carbon nanotube	24.0	[8]
Active carbon	26.0	[8]

Table 8. Surface nitrogen composition of AC-180 and creatinine adsorbed 180-AC derived from XPS.

Sample	N%					
	N_{total}	N1	N2	N3	N4	N5
180-AC	0.74	—	—	0.33	—	0.41
Creatinine adsorbed 180-AC	2.58	0.91	0.70	0.57	0.15	0.41