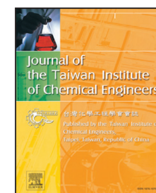
Journal of the Taiwan Institute of Chemical Engineers 66 (2016) 347–356

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice



Adsorption of creatinine on active carbons with nitric acid hydrothermal modification

Yuhe Cao[a], Yan Gu[b], Keliang Wang[a], Xiaomin Wang[a], Zhengrong Gu[a,*], Tyler Ambrico[c], Maria Andrea Castro[d], Joun Lee[e], William Gibbons[f], James A. Rice[g]

[a] *Agricultural and Biosystems Engineering Department, South Dakota State University, Brookings, SD 57007, USA*
[b] *Institute of Chemical Industry of forest Product, NanJing, Jiangsu, China*
[c] *Department of Physics and Astronomy, Stony Brook University, Stony Brook, NY, USA*
[d] *Department of Chemistry, University of Iowa, Iowa City, IA, USA*
[e] *Central Microscopy Research Facility, University of Iowa, Iowa City, IA, USA*
[f] *Department of Biology and Microbiology, South Dakota State University, Brookings, SD, USA*
[g] *Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD, USA*

ARTICLE INFO

Article history:
Received 18 February 2016
Revised 24 May 2016
Accepted 9 June 2016
Available online 4 July 2016

Keywords:
Creatinine
Active carbon
Nitric acid
Hydrothermal
Adsorption

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 N_2 adsorption, temperature programmed desorption (TPD), Fourier Transform Infrared spectroscopy (FTIR), and X-ray photoelectron spectrometer (XPS). It indicated that 4 M HNO_3 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.

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1. 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

* Corresponding author. Tel.: +1 6056885372; fax: +1 6056886764.
E-mail address: Zhengrong.gu@sdstate.edu (Z. Gu).

http://dx.doi.org/10.1016/j.jtice.2016.06.008
1876-1070/Published by Elsevier B.V. on behalf of Taiwan Institute of Chemical Engineers.

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 HNO_3 at 120 °C, 150 °C and 180 °C, respectively. To our knowledge, similar research has not been reported so far.

2. Materials and methods

2.1. Materials

HNO_3 and creatinine (Assay Percent Range: 99+%, $C_4H_7N_3O$) 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 4 M HNO_3 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 h. The wet AC was dried at 105 °C for 24 h. 3 g of the dried AC was reacted with 40 ml 4 M HNO_3 in a sealed PTFE reactor (50 ml) at 120, 150, and 180 °C for 1 h, 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 N_2 using an ASAP 2020 Micropore Analyzer. The total pore volume was determined at relative pressure 0.995 P_0, 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 N_2 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 cm^3/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 Kα X-ray (1486.6 eV) at 150 W (accelerating voltage 15 kV, emission current 10 mA) was projected 45° to the sample surface and the photoelectron data was collected at takeoff angle of $\theta = 90°$. 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 1 s, O 1 s, and N 1 s were taken at pass energy of 20 eV with 0.1 eV steps and a dwell time of 1000 ms. 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 1 s 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 place 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:

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

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.

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