



Enhanced mercury ion adsorption by amine-modified activated carbon

Jianzhong Zhu^a, John Yang^{a,*}, Baolin Deng^b

^a Center of Environmental Sciences, Lincoln University of Missouri, Jefferson City, MO 65102, USA

^b Department of Civil and Environmental Engineering, University of Missouri, Columbia, MO 65211, USA

ARTICLE INFO

Article history:

Received 2 June 2008

Received in revised form

24 November 2008

Accepted 25 November 2008

Available online 3 December 2008

Keywords:

Activated carbon

APTES

Surface modification

Mercury adsorption

ABSTRACT

Mercury (Hg) is one of the most toxic metals found in water and sediments. In an effort to develop an effective adsorbent for aqueous Hg removal, activated carbon (AC) was modified with an amino-terminated organosilicon (3-aminopropyltriethoxysilane, APTES). Surface properties of the APTES-modified AC (MAC) were characterized by the scanning electron microscopy in conjunction with the energy-dispersive spectroscopy (SEM-EDS), the Fourier transform infrared spectroscopy (FT-IR), and potentiometry. The impacts of solvent, APTES concentration, reactive time and temperature on the surface modification were evaluated. The aqueous Hg adsorptive kinetics and capacity were also determined. Results demonstrated that the strong Hg-binding amine ligands were effectively introduced onto the AC surfaces through the silanol reaction between carbon surface functional groups (–COOH, –COH) and APTES molecules. The modification lowered the pH at the point of zero charge (pH_{pzc}) to 4.54 from 9.6, favoring cation adsorption. MAC presented a faster rate of the Hg (II) adsorption and more than double adsorptive capacity as compared with AC.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Mercury (Hg) is one of the extremely toxic metals in the environment that can cause irreversible neurological damage in human [1]. The World Health Organization (WHO) recommends a maximum human Hg uptake of 0.3 μg per week and a maximum acceptable concentration of 1 $\mu\text{g L}^{-1}$ in drinking water [2]. The USEPA permitted discharge limit of wastewater for total Hg is 10 $\mu\text{g L}^{-1}$ while the limit for drinking water is 2 $\mu\text{g L}^{-1}$ [3]. Japan Ministry of the Environment establishes even more strict limits at 5 and 0.5 $\mu\text{g L}^{-1}$ [4], respectively. Therefore, the removal of mercury to the acceptable concentration is a challenge in drinking water and wastewater treatment [5]. Traditional methods that have been used to remove and/or separate aqueous Hg ions include sulfide precipitation, ion exchange, alum and iron coagulation [6], these methods, however, often have a low removal efficiency and/or have a need for additional treatment that potentially creates more sludge during the removal process [7]. Especially, the removal is ineffective when the Hg concentration is low. Thus, there is a strong incentive to develop novel adsorbents that have high efficiency and selectivity for Hg ion removal from aqueous media.

Activated carbon (AC) is a common adsorbent that is often used for aqueous metal removal because of its excellent porous structures, specific surface properties, reusability, minimal costs, and

environmentally benign nature [8]. The surface chemical modification of AC has been recognized as an effective approach for enhancing metal removal from aqueous media [9]. For example, quaternized poly(4-vinylpyridine) [10] and iron oxides [11] have been used to modify carbon surfaces for arsenic treatment. According to the Hard-Soft Acid-Base (HSAB) theory [12], mercuric ions interact strongly with nitrogen-containing ligands such as pendant urea on resin [13], dipyritylamide [14] and polythiourea on charcoal [15], which have recently been used for the Hg removal from aqueous solutions [13]. Thus it could be reasonably assumed that additions of N-containing ligands on the AC surface would substantially enhance the efficacy of Hg removal from aqueous media [14,15]. This study attempts to modify the AC surface with an amine-terminated organosilicon (3-aminopropyltriethoxysilane, APTES) and create new N-immobilized Lewis basic centers [16] for enhanced sorption of metals such as Hg ions from aqueous solutions.

While the modification of the AC surface by an organosilane has not been reported yet, APTES molecule containing active-NH₂ terminal groups was reported to strongly interact with hydroxyl groups and hydrolyzed head groups [17,18]. The mechanisms of such interactions were well documented [19]. APTES molecule can react not only with active functional groups (e.g. –OH) on the inorganic substrate, but also with another APTES molecule through three hydrolyzed ethoxy groups, resulting in a polymerized network [20,21]. Therefore, APTES can potentially form a three-dimensional multilayer network on the AC surface through covalent bonds between the surface carboxyl/hydroxyl groups and

* Corresponding author. Tel.: +1 573 681 5383; fax: +1 573 681 5548.
E-mail address: yangj@lincolnu.edu (J. Yang).

the APTES-NH₂ group [22,23] and/or physical attractions between APTES molecule and substrates [24,25]. Such modification of the AC surface easily converts the surface carboxyl/hydroxyl groups to the high Hg-affinity amine groups under ambient conditions [10].

This study is to modify the AC surface using an amine-terminated silylating agent (3-aminopropyltriethoxysilane, APTES) for substantially enhancing the AC adsorptive capacity for aqueous Hg ions. The effects of several reaction variables such as APTES concentration, reaction temperature and time on the surface modification were evaluated. The modified AC surface was characterized by the scanning electron microscopy in conjunction with the energy-dispersive spectroscopy (SEM-EDS), the Fourier transform infrared spectroscopy (FT-IR), and potentiometry. The removal efficacy of aqueous Hg ions was determined by batch experiments of adsorptive kinetics and equilibrium isotherm.

2. Experimental procedures

2.1. Modification of activated carbon

Scheme of the surface modification of activated carbon by 3-aminopropyltriethoxysilane (APTES, 99%, Aldrich) is shown in Fig. 1 [10,17,20,24]. Activated carbon (NORIT Dacro 20x40L, surface area of 650 m² g⁻¹, density of 400 g L⁻¹, particle diameter of 0.42–1.0 mm) was initially mixed with a solvent [deionized water, ethanol (99.5%, Aldrich) or toluene (98%, Aldrich)] at a 1:10 solid/liquid (S/L) ratio and stirred. APTES was then added to the mixture at a rate of 2%, 3%, 4%, or 5%, respectively, and the APTES-AC mixture was sonicated for 10 min. The suspension was adjusted to pH 3–4 using concentrated HCl (36%, Aldrich), kept for 1 h at room temperature, and subsequently refluxed for 4, 6, 12, or 24 h under each of 50, 70, 90 or 110 °C. Upon completion of the reaction time, the carbon was separated from the aqueous phase by centrifugation, washed thoroughly with ethanol or toluene and subsequently deionized water until the absence of free Cl ions (as tested by 0.01N AgNO₃ solution) and non-reacted silane (as washed with dried toluene at room temperature for 20 min). The APTES-modified carbon (MAC) was vacuum-dried under 40 °C overnight

and stored in a dark container until analyses. The parameters that may affect the efficacy of the modification (solvent type, reaction temperature, APTES concentration, reaction time) were evaluated to determine the optimal conditions of modification.

2.2. Surface characterization

The modified carbon samples were characterized by scanning electron microscopy (SEM) to evaluate the alterations of surface morphology by the treatments. The samples were mounted using double-side silver tapes on 1-cm diameter aluminum stubs, coated with 10-μm carbon layer, and analyzed with the AMRAY 1600 scanning electron microspectrometer operated at 5–20 keV. The surface elemental composition was determined by the energy-dispersive spectroscopy (EDS). The surface organic-inorganic ligands were qualitatively measured using a Fourier transform infrared spectroscopy (FT-IR). Sample discs were prepared by mixing 1 mg of the samples with 500 mg of KBr (Merck) in an agate mortar and scanned in a range from 4000 to 400 cm⁻¹ using a Nicolet 4700 FT-IR spectrometer. The surface charges and the H⁺-binding isotherm of the samples were examined by the potentiometric titration. The samples, 0.1000 g, were suspended in 50 mL of 0.01 M NaNO₃ solution that was acidified with 2–5 mL of 0.1 M HNO₃ solution. The suspensions were continuously purged with purified nitrogen gas to eliminate atmospheric CO₂ and stirred throughout the measurement. The titration was performed with 0.1 M NaOH solution using an automatic Metrohm 716 DMS Titrimo titrator at the pH range of 2.0–11.0. The pH was measured after 10 min of equilibration. Unmodified activated carbon was included as the control in all analyses.

2.3. Adsorption experiments

Adsorption kinetics and equilibrium isotherms were studied to evaluate the efficacy of the modification in context of the rate and capacity of the Hg removal by the activated carbons. A standard solution of 1000 mg Hg²⁺ L⁻¹ was prepared by dissolving 1.3540 g HgCl₂ in double distilled water, acidified with 5 mL of concentrated

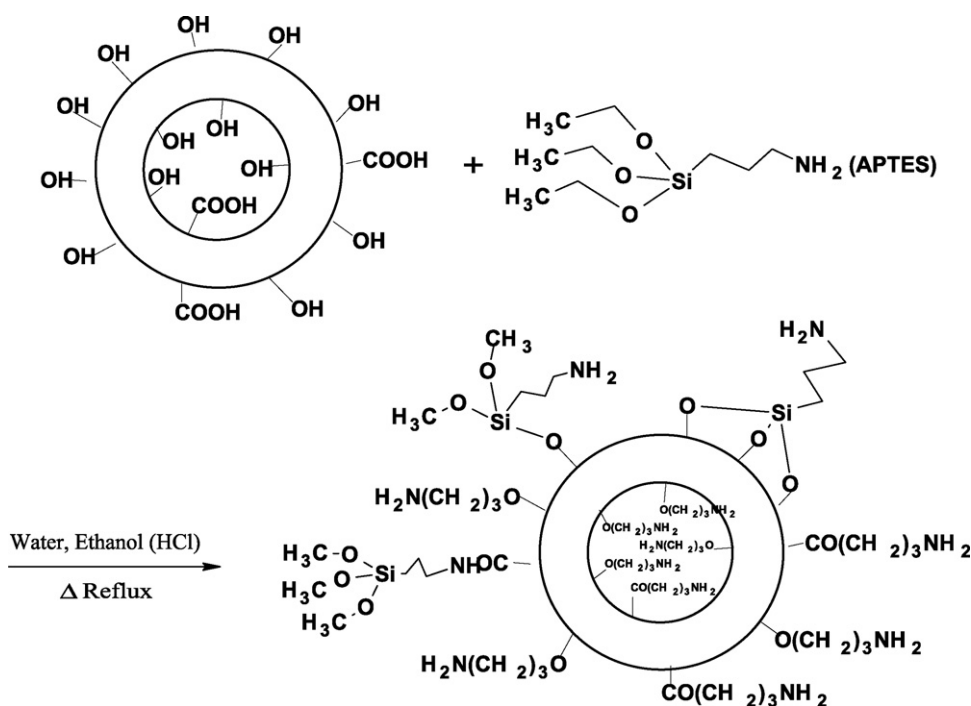


Fig. 1. Schematic illustration of the surface modification of activated carbon (AC) by 3-aminopropyltriethoxysilane (APTES).

HNO₃ and diluted to 1000 mL volume. A buffer solution (0.01 M KH₂PO₄-NaOH, pH ~6) was also used for the adsorptive experiments. In the kinetics study, 0.1000 g of the carbon was added to 500-mL glass flask containing 300 mL of the pH ~6 buffer solution [26] with initial Hg concentration of 40 mg L⁻¹. The suspension was shaken at 150 rpm and 25 °C. The solution, 4 mL, was sampled by a 10-mL plastic syringe at each of 2, 5, 10, 30, 60 min, and then every 60 min until 1440 min, respectively. The sample solutions were passed through a Whatman 0.45-μm filter (Fisher Scientific), acidified with 2–3 drops of concentrated HNO₃ to stabilize Hg²⁺ ions. The aqueous Hg was analyzed by a VARIAN ICP-AOE spectrometer. The solution pH was also measured using an Orion 525A pH meter. The equilibrium isotherm was established by adding predetermined carbons to 60-mL glass bottles containing the pH (~6.0) buffer solution with the Hg concentration of 80 mg L⁻¹. The suspension was shaken at 150 rpm and 25 °C for 24 h, and the solution was then sampled and analyzed for Hg concentration. All experiments were conducted in duplicate. During the Hg analyses, the ICP-AOE was automatically calibrated every 10-sample run using a mercury standards (SPEX Certiprep, NJ). The standard recovery was observed in the range of 90–110% for a 1 mg L⁻¹ mercury spiking solution, and the variation among replicated samples was within 10%, which was acceptable when the variation of instrumental stability and operation procedures were considered.

3. Results and discussions

3.1. Effects of reaction conditions

3.1.1. Effect of reaction temperature

The APTES modification could be affected by the number of factors such as temperature, reaction time, and reactant concentrations. Measurements of the Hg²⁺ adsorption indicated that the efficacy of the modification varied with reaction conditions (Table 1). When the reactions occurred under variable temperatures (50, 70, 90 or 110 °C), the MAC adsorptive capacity for aqueous Hg ions was found to be the highest at 70 °C. The grafting of the APTES functional groups onto the AC surface depends on thermal process of the molecules. Increasing temperature might have enhanced the interactions of APTES molecules with the AC surface functional groups (e.g. -COOH, -OH), facilitating APTES binding to the AC surface [27]. APTES molecule contains an active amine terminal group that is able to form a hydrogen bond with multiple hydroxylated head groups among APTES molecules and/or hydroxyl groups on the AC surface, thus resulting in cyclic structures and a complex loose network [28]. However, under relatively high temperature (>70 °C), the hydrogen bond formed among APTES molecules or between APTES and the AC surface could be broken, allowing more silanol groups to condense with each other and form siloxane linkages, consequently tightening the three-dimensional network [29]. When AC is in contact with APTES, APTES molecules can diffuse or penetrate into the AC surfaces, with which the AC surface could be tightened by the additional crosslinking [30]. A thermal process would help tighten the network or increase the crosslinking among APTES molecules. However, measurements did not show that a higher temperature would lead to a large Hg adsorption capacity

or increase the characteristic peaks of the function groups in FT-IR patterns.

3.1.2. Effect of reaction time and APTES concentration

Experimental results indicated that optimal reaction time for the APTES modification was around 6 h and increasing reaction time would not improve the Hg²⁺ removal by MAC (Table 1). The impact of the APTES concentration showed that 2–3% APTES would achieve the highest Hg²⁺ removal capacity by MAC (Table 1). The AC to APTES ratio is directly related to the moles of the active function groups. At the ethanol:AC:APTES ratio of 50:5:1 or 50:5:1.5, amine groups could be bound to inside walls of AC pores without forming the polymerized products, which resulted in a high Hg²⁺ removal capacity of 122.8 or 118.4 mg g⁻¹. When the APTES ratio was >2 (e.g. 5%), the adsorption capacity of the AC was lowered to 90.76 mg g⁻¹. The reduction of the adsorption could be due to partial blockage of the AC micropores by the formation of polymerized APTES products, which may affect the Hg ion diffusion into AC inside walls or prevent the Hg complex formation on the surface.

3.1.3. Effect of reaction media

Type of solvent used as reaction media during the APTES modification has been reported to influence the interactions between APTES molecules and the AC surface. Water could facilitate initial hydrolysis of APTES or at the AC surface, depending on the amount of water present in the system. Hydrolysis of the ethoxy groups was reported to form a polymer composed of polysiloxane [31]. Excessive water in the system would promote the polymerization of APTES in solvent phase [32], which prevents APTES molecules from further reacting with or binding to the AC surface. However, the interactions between APTES molecules and the AC surface could be enhanced in ethanol or toluene solvent due to the nucleophilic attack of APTES amine groups [33,34], which promotes binding of the amine groups to the AC surface. Hydrolysis of silane would be a critical step driving the APTES attachment to the AC surface through siloxane bonds. The siloxane bond forms through the interactions of ethoxy groups with neighbors H-bonded to the surface or with free APTES molecules in solution. The proposed mechanism is that the hydrolysis of APTES (Fig. 2a) at the hydroxylic AC surface generates a silanetriol, which then physisorbs onto the surface via hydrogen bonding, ultimately forming cross-linked covalent bonds in both C_{Substrate}-O-Si_{silane} (AC-APTES) and Si_{silane}-O-Si_{silane} (APTES-APTES) in the presence of HCl [35]. The formation of siloxane cross-links by APTES through H-bonding and H-bond acceptor is the driving force of the surface reactions leading to the physisorption of APTES to the AC surface (Fig. 2b and c) [36,37]. Thus, the -NH sites on the MAC surface would potentially contribute to high affinity and capacity of the Hg (II) adsorption.

3.2. Surface characterization

As shown in Fig. 3, there are obvious morphological differences of the SEM micrographs of AC, MAC and Hg-adsorbed MAC (Hg-MAC). AC had many bright micropores with some distortions of shape on the surface (Fig. 3a), containing sodium, molybdenum, silicon and aluminum (Fig. 3d). Morphological features of MAC

Table 1
Effects of reaction temperature, time, and APTES concentration on the Hg²⁺ adsorption.

| Factors | Effect of temperature (°C) ^a | | | | Effect of reaction time (h) ^b | | | | APTES (%) ^c | | | |
|-----------------------|---|--------|-------|-------|--|-------|--------|--------|------------------------|--------|-------|-------|
| | 50 | 70 | 90 | 110 | 4 | 6 | 12 | 24 | 2 | 3 | 4 | 5 |
| Q _e (mg/g) | 74.56 | 118.98 | 92.41 | 89.54 | 81.90 | 122.8 | 108.69 | 101.12 | 122.8 | 118.39 | 98.48 | 90.76 |

^a Ethanol:AC:APTES ratio = 50:5:1, t = 6 h.

^b Ethanol:AC:APTES ratio = 50:5:1, T = 70 °C.

^c t = 6 h, T = 70 °C.

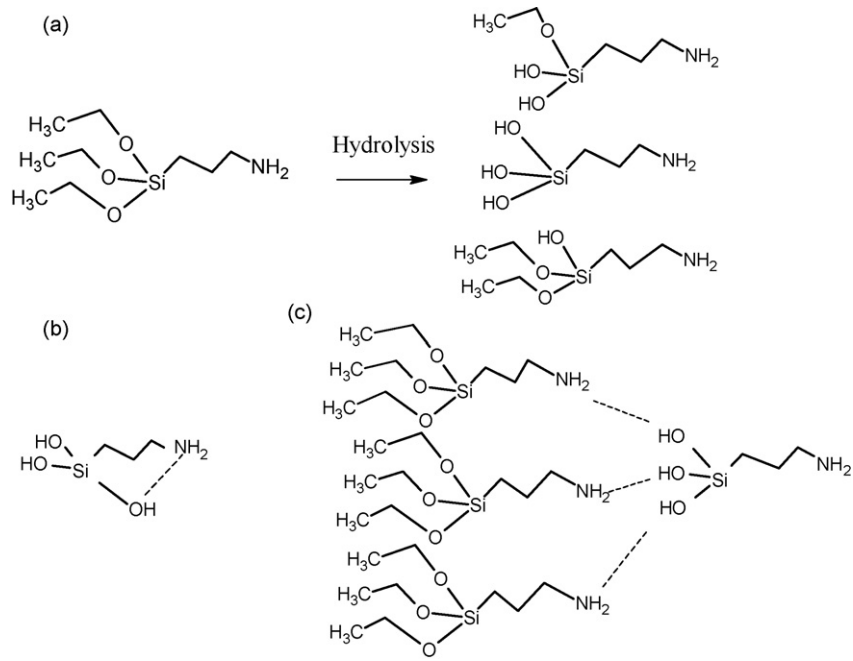


Fig. 2. APTES molecular hydrolysis (a), possible inter-molecular hydrogen bonding interaction (b) and intra-molecular AC-OH-NH₂ bridges (c) in solution.

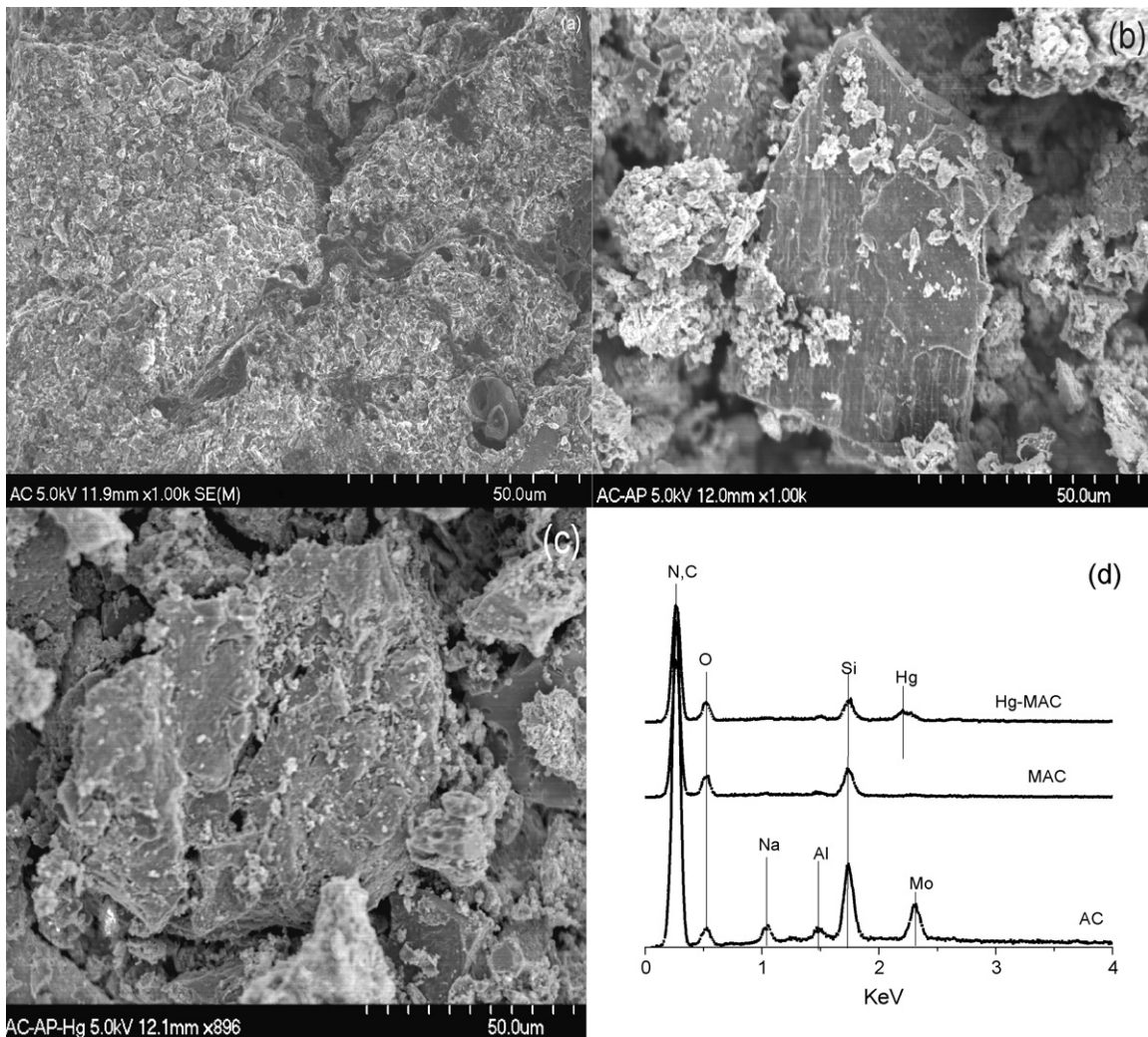


Fig. 3. SEM micrographs of AC (a), MAC (b), Hg-MAC (c), and EDS spectra (d).

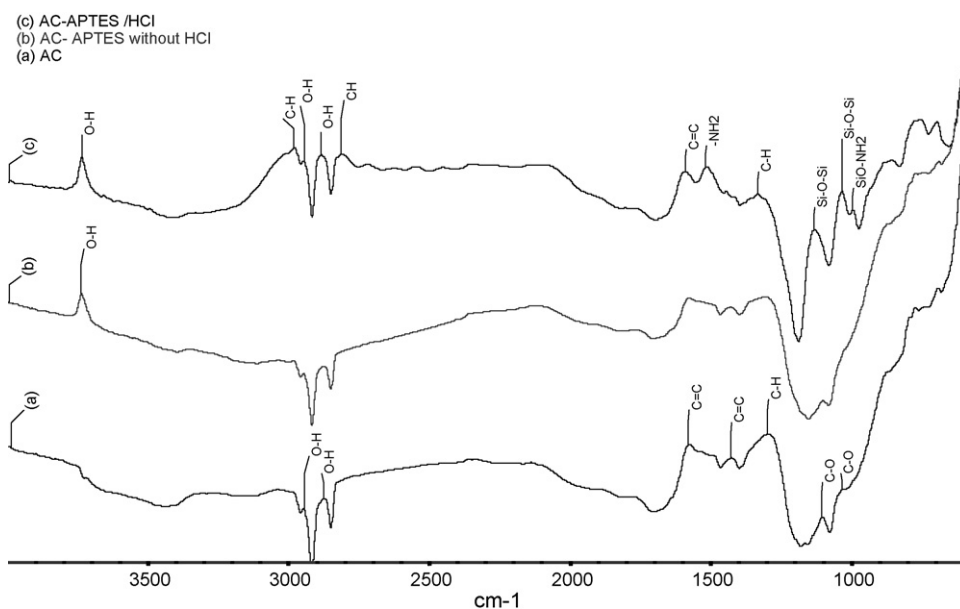


Fig. 4. FT-IR spectra of activated carbons before and after modification.

were monoliths together with thin film, rough and porous surface (Fig. 3b). The porous structures of MAC may result from the bridging linkage of APTES molecules among the amine groups in the MAC surface through the intra- and/or inter-molecular cross-linking connections, which may generate new binding sites in interior walls of the micropores and contribute to homogeneous Hg binding, as evidenced by the disappearance of the metal peaks in the EDS pattern (Fig. 3d). The Hg-MAC exhibited a fractured and smooth surface in the presence of very high Hg (Fig. 3c and d).

The FT-IR spectrum presented in Fig. 4. showed that, in comparison with the AC spectrum, there were several new bands appeared on the MAC surface at 3797 cm^{-1} and $2949\text{--}2886\text{ cm}^{-1}$, which are identified as the O–H stretching vibration mode of water on silica surface and characteristic of CH stretching vibration mode, respectively [38,39]. Additional band at 999.5 cm^{-1} remained unknown, which probably relates to the H-bonded Si–O stretching mode of surface silanol Si–O bonded to --NH_2 group [40,41]. The band at 1517.7 cm^{-1} was assigned as --NH_2 scissors frequencies [39] and 1132 cm^{-1} or 1035 cm^{-1} as Si–O–Si stretching [42]. The MAC without HCl treatment presented only a band at 3797 cm^{-1} . Results suggested that HCl plays a catalytic role for the hydrolysis of the AC surface, causing silanol functionality toward chlorosilanes, and demonstrated that the amine groups of APTES had been successfully introduced onto the AC surfaces, which would generate new sites for the Hg adsorption [43].

Proton-binding isotherm of AC and MAC established by a potentiometric titration is presented in Fig. 5. The amounts of protons adsorbed (Q) were calculated using Eq. (1) [44]:

$$Q = \frac{V_0 + V_t}{m} ([\text{H}]_i - [\text{OH}]_i - [\text{H}]_e + [\text{OH}]_e) \quad (1)$$

where V is the volumes of background electrolyte and titrant added, and m is the mass of adsorbent. Subscripts i and e refer to initial and equilibrium concentrations. The equilibrium proton concentration was calculated from the measured pH using an activity coefficient estimated from the Davis's equation. The isotherm showed more surface acidity of MAC than AC. The pH at the point of zero charge (pH_{pzc}) was determined to be 4.55 for MAC and 9.6 for AC. Decreased pH_{zpc} induced by the modifications implied that APTES ligands had been incorporated onto the AC surface, which made the AC surface more negatively charged and would favor the surface

electrostatic interactions with aqueous metal cations or surface Hg adsorption.

3.3. Mercury adsorption

The percentage of Hg removal from aqueous phase as a function of time shown in Fig. 6 illustrated that, within 24 h, MAC exhibited a significantly higher adsorption rate than AC and the adsorption equilibrium was reached within 30 min. A 40–50% removal capacity was achieved during the first hour, and the adsorption then gradually reached a steady state. The kinetically rapid adsorption by MAC implied the generation of strong Hg-binding sites of the MAC surface.

An adsorption isotherm was established to determine the Hg sorption capacity of the activated carbons (Fig. 7). In the isotherm, the Hg concentration retained by the carbons was calculated using Eq. (2)

$$Q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

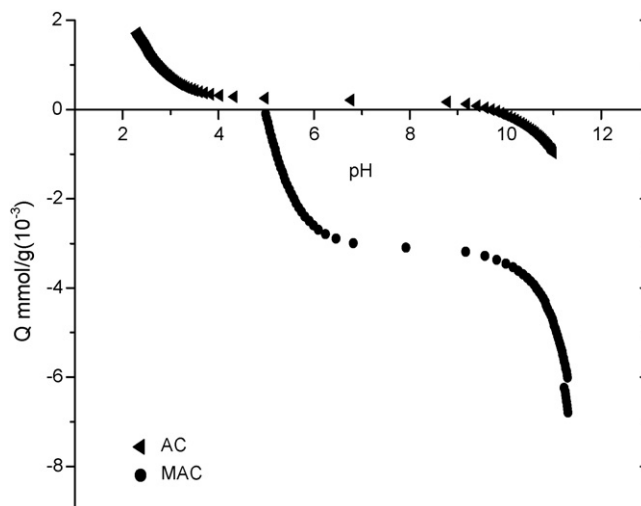


Fig. 5. Proton-binding isotherm of the AC and MAC.

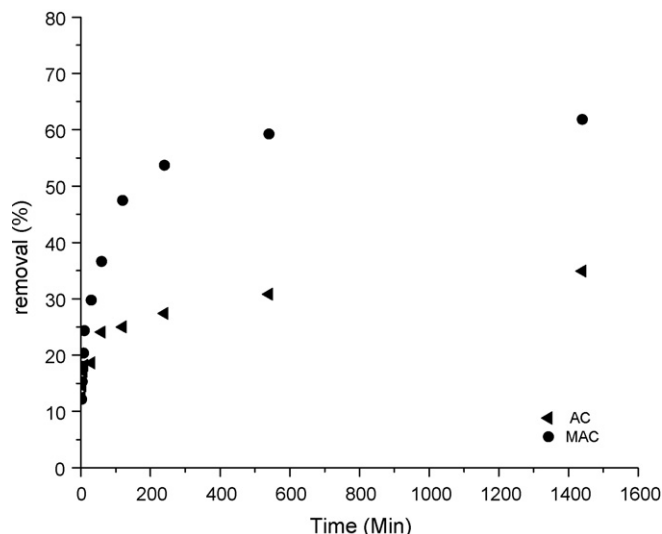


Fig. 6. Removal of aqueous Hg^{2+} as a function of contact time. (Solid loading = 3.33 g L^{-1} ; $C_0 = 41.59 \text{ mg L}^{-1}$; buffer (pH ~ 6.0); and $T = 25^\circ \text{C}$.)

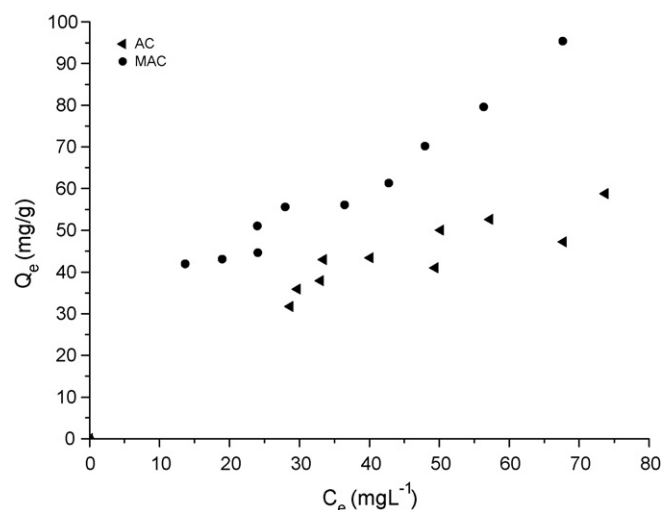


Fig. 7. Equilibrium isotherm of the Hg^{2+} adsorption by AC and MAC. ($C_0 = 83.55 \text{ mg L}^{-1}$; $t = 24 \text{ h}$; buffer (pH ~ 6.0); $T = 25^\circ \text{C}$.)

where C_0 and C_e are the initial and equilibrium concentrations of Hg ion in solution, V is the volume and W is the weight of the carbon. The amount of the Hg adsorbed by MAC at equilibrium was found more than double than that of AC. This indicated that the surface modifications by the APTES treatments had significantly enhanced the capacity of activated carbon to bind aqueous Hg ions with the surface functional ligands. High adsorptive capacity was accomplished by strong Hg-binding to $-\text{NH}_2$ and $-\text{NH}$ groups formed on the AC surface as a result of APTES treatment.

4. Conclusions

This study demonstrated that a new Hg (II) adsorbent was successfully synthesized by modifying activated carbon using 3-aminopropyltriethoxysilane (APTES). The chemical modification was most effective with 2–3% APTES in ethanol or toluene reacted at 70°C and for about 6 h. The APTES treatment altered the morphology and physicochemical properties of activated carbon, making the surface more negatively charged and more hydrophilic with a lower pH_{pzc} . The modified activated carbon (MAC) exhibited much higher adsorption rate and capacity for aqueous mercury. Enhanced

adsorptive rate and capacity were accomplished by generating new strong Hg-binding sites on the modified activated carbon surface through the reactions between APTES and the AC surface.

Acknowledgements

Authors would thank Mr. Lou Ross and Dr. Keith Goynes at University of Missouri–Columbia for their technical assistance in the SEM-EDS and FT-IR analyses. Also thanks go to Dr. Ikem at Lincoln University of Missouri for his supports in ICP analyses. Activated carbon used for this study was provided by American Norit Co. Inc. Financial supports for this research were provided by the USEPA-NCER-STAR (RD831071), the USDA-CSREES (MOX-YANG) to Lincoln University of Missouri and the US-Department of Energy (DE-FC26-02NT41607) to University of Missouri.

References

- [1] F.F. William, W.C. Thomas, Mercury and monomethylmercury: present and future concerns, *Environ. Health Perspect.* 96 (1991) 59–166.
- [2] C.W. Forster, *Biosorbents for Metal Ions*, Taylor & Francis, 1997.
- [3] USEPA, National Primary Drinking Water Standards, US Environmental Protection Agency, Washington, DC, 2001.
- [4] Y. Takahashi, K. Watanuki, S. Kubota, O. Wada, Y. Arikawa, S. Naito, S. Monma, T. Hirano (Eds.), *An Encyclopedia of Water*, Maruzen, Tokyo, 2001.
- [5] S. Oha, T. Kang, H. Kim, Preparation of novel ceramic membranes modified by mesoporous silica with 3-aminopropyltriethoxysilane (APTES) and its application to Cu^{2+} separation in the aqueous phase, *J. Membr. Sci.* 301 (2007) 118–125.
- [6] J.W. Patterson, *Wastewater Treatment Technology*, Ann Arbor Science Publishers, Ann Arbor, MI USA, 1975.
- [7] P.K. Jal, S. Patel, B.K. Mishra, Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions, *Talanta* 62 (2004) 1005–1028.
- [8] F. Rodriguez-Reinoso, The role of carbon materials in heterogeneous catalysis, *Carbon* 36 (1998) 159–175.
- [9] J.P. Chen, S.N. Wu, K.H. Chong, Surface modification of a granular activated carbon by citric acid for enhancement of copper adsorption, *Carbon* 41 (2003) 1979–1986.
- [10] J. Fang, Z. Gu, D. Gang, C. Liu, E. Ilton, B. Deng, Cr(VI) removal from aqueous solution by activated carbon coated with quaternized poly(4-vinylpyridine), *Environ. Sci. Technol.* 41 (2007) 4748–4753.
- [11] Z. Gu, B. Deng, J. Yang, Synthesis and evaluation of iron-containing ordered mesoporous carbon (FeOMC) for arsenic adsorption, *Micropor. Mesopor. Mater.* 102 (2007) 265–273.
- [12] R.G. Pearson, Hard and soft acids and bases, *J. Am. Chem. Soc.* 85 (1963) 3533.
- [13] N. Bicač, D.C. Sherrington, S. Sungur, N. Tan, A glycidyl methacrylate-based resin with pendant urea groups as a high capacity mercury specific sorbent, *React. Funct. Polym.* 54 (2003) 141–147.
- [14] K. Wurst, G.K. Bonn, Dipyrindyl amide-functionalized polymers prepared by ring-opening-metathesis polymerization (ROMP) for the selective extraction of mercury and palladium, *J. Am. Chem. Soc.* 120 (1998) 2790–2797.
- [15] A. Sasaki, Y. Kimura, Preparation of polythiourea-immobilized activated charcoal and its utilization for selective adsorption of mercury(II) ion. Studies on functionalization of polymers by reactive processing, *Nippon Kagaku Kaishi* 5 (1997) 880–886.
- [16] A.R. Cestari, E.F.S. Vieira, E.C.N. Lopes, R.G. da Silva, Kinetics and equilibrium parameters of Hg(II) adsorption on silica-dithizone, *J. Colloid Interface Sci.* 272 (2004) 1271–1276.
- [17] H. Elwing, I. Lundstroem, Structure of 3-aminopropyl triethoxy silane on silicon oxide, *J. Colloid Interface Sci.* 147 (1991) 103–111.
- [18] M. Etienne, A. Walcarius, Analytical investigation of the chemical reactivity and stability of aminopropyl-grafted silica in aqueous medium, *Talanta* 59 (2003) 1173–1188.
- [19] L.L. Crowe, Reversible Attachment of Organic Dyes Organic Dyes to Silica Surface through Meijer-type Quadruple Hydrogen Bonding, Georgia Institute of Technology, 2006.
- [20] S. Flink, F.C.J.M. Van Veggel, D.N. Reinhoudt, Functionalization of self-assembled monolayers on glass and oxidized silicon wafers by surface reactions, *J. Phys. Org. Chem.* 14 (2001) 407–415.
- [21] K.M.R. Kallury, P.M. Macdonald, M. Thompson, Effect of surface water and base catalysis on the silanization of silica by (aminopropyl) alkoxy silanes studied by X-ray photoelectron spectroscopy and ^{13}C cross-polarization/magic angle spinning nuclear magnetic resonance, *Langmuir* 10 (1994) 492–499.
- [22] M.E. McGovern, K.M.R. Kallury, M. Thompson, Role of solvent on the silanization of glass with octadecyltrichlorosilane, *Langmuir* 10 (1994) 3607–3614.
- [23] D. Kowalczyk, S. Słomkowski, M.M. Chehimi, M. Delamar, Adsorption of aminopropyltriethoxy silane on quartz: an XPS and contact angle measurements study, *Int. J. Adhes. Adhes.* 16 (1996) 227–232.

- [24] F. Zhang, M.P. Srinivasan, Self-assembled molecular films of aminosilanes and their immobilization capacities, *Langmuir* 20 (2004) 2309–2314.
- [25] A.T. Simon, T. Cohen-Bouhacina, M.C. Porte, Study of two grafting methods for obtaining a 3-aminopropyltriethoxysilane monolayer on silica surface, *J. Colloid Interface Sci.* 251 (2002) 278–283.
- [26] M.E. Mahmoud, M.M. Osman, M.E. Amer, Selective pre-concentration and solid phase extraction of mercury(II) from natural water by silica gel-loaded dithione phases, *Anal. Chim. Acta* 415 (2000) 33–40.
- [27] Z.P. Yao, R. Bengt, Surface modification by continuous graft copolymerization. III. Photoinitiated graft copolymerization onto poly(ethylene terephthalate) fiber surface, *J. Appl. Polym. Sci.* 41 (1990) 1459–1467.
- [28] L.D. White, C.P. Tripp, Reaction of (3-aminopropyl) dimethylethoxysilane with amine catalysts on silica surfaces, *J. Colloid Interface Sci.* 232 (2000) 400–407.
- [29] L.N. Bui, M. Thompson, N.B. McKeown, A.D. Romaschin, P.G. Kalman, Surface modification of the biomedical polymer poly (ethylene terephthalate), *Analyst* 118 (1993) 463–474.
- [30] S.H. Choi, B.N. Zhang, Suppress polystyrene thin film dewetting by modifying substrate surface with aminopropyltriethoxysilane, *Surface Sci.* 600 (2006) 1391–1404.
- [31] H.J. Martin, K.H. Schulz, J.D. Bumgardner, K.B. Walters, XPS Study on the use of 3-aminopropyltriethoxysilane to bond chitosan to a titanium surface, *Langmuir* 23 (2007) 6645–6651.
- [32] A. Howarter, P.Y. Jeffrey, Optimization of silica silanization by 3-aminopropyltriethoxysilane, *Langmuir* 22 (2006) 11142–11147.
- [33] C.P. Tripp, M.L. Hair, An Infrared study of the reaction of ctadecyltrichlorosilane with silica, *Langmuir* 8 (1992) 1120–1126.
- [34] S.A. Kanan, W.T.Y. Tze, C.P. Tripp, Method to double the surface concentration and control the orientation of adsorbed (3-aminopropyl) dimethylethoxysilane on silica powders and glass slides, *Langmuir* 18 (2002) 6623–6627.
- [35] J. Sagiy, Organized monolayers by adsorption. I. Formation and structure of oleophobic mixed monolayers on solid surfaces, *J. Am. Chem. Soc.* 102 (1980) 92.
- [36] S.A. Biltresse, M. Marchand-Brynaert, Cell adhesive PET membranes by surface 16 grafting of RGD peptidomimetics, *J. Biomater.* 26 (2005) 4576–4587.
- [37] I.K. Bisson, M. Kosinski, S. Ruault, B. Gupta, J. Hilborn, F. Wurm, P. Frey, Acrylic acid grafting and collagen immobilization on poly (ethylene terephthalate) surfaces for adherence and growth of human bladder smooth muscle cells, *Biomaterials* 23 (2002) 3149–3158.
- [38] L.N.H. Arakaki, C. Airoidi, Ethylenimine in the synthetic routes of a new silylating agent: chelating ability of nitrogen and sulfur donor atoms after anchoring onto the surface of silica gel, *Polyhedron* 19 (2000) 367–373.
- [39] D. Lin-Vien, N.B. Colthup, W.G. Fateley, J.G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, London, 1991.
- [40] R.W. Mitchell Jr., J.C. Burr, J.A. Merritt, Vibrational spectra of normal, imine-deuterated and 15N ethyleneimine, *Spectrochim. Acta* 23A (1967) 195.
- [41] C.P. Tripp, M.L. Hair, Chemical attachment of chlorosilanes to silica: a two-step amine-promoted reaction, *J. Phys. Chem.* 97 (1993) 5693.
- [42] C. Airoidi, E.F.C. Alcantara, Chemisorption of divalent cations on N-(2-pyridyl) acetamide immobilized on silica gel—a thermodynamic study, *J. Chem. Thermodyn.* 27 (1995) 623–632.
- [43] J.A. Howarter, P.Y. Jeffrey, Surface modification of polymers with 3-aminopropyltriethoxysilane as a general pretreatment for controlled wettability, *Macromolecules* 40 (2007) 1128–1132.
- [44] A.M.P. Puziy, I. Olga, J.A. Ritter, A.D. Ebner, C.E. Holland, Elucidation of the ion binding mechanism in heterogeneous carbon-composite adsorbents, *Carbon* 39 (2001) 2313–2324.