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Modification of Activated Carbon by Polyaniline for Enhanced Adsorption of Aqueous Arsenate

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A raw granular activated carbon (RGAC) is modified by polyaniline to improve arsenate adsorption. It is found that the modification does not change the specific surface area. The content of the aromatic ring structures and nitrogen-containing functional groups on the modified GAC (MGAC) is increased. The surface positive charge density is dramatically increased in acidic solutions. The adsorption of As(V) onto both sorbents is highly pH dependent. The modification broadens the optimal pH range for the arsenate adsorption: pH of 3.0−6.8 and 4.0−6.6 for the MGAC at initial arsenic concentrations of 0.15 and 8.0 mg L^{-1} vs pH 6.0 and 6.5 for the RGAC at the same concentrations. The maximum adsorption capacity at an optimal pH of 5.5 is enhanced by 84%. The MGAC is able to greatly remove the arsenic at a trace level; the concentration of treated solution is far below the U.S. EPA standard. The presence of humic acid does not have a great impact on the arsenic adsorption dynamics. The modification significantly enhances the adsorption of humic acid onto the carbon. X-ray photoelectron spectroscopy analysis demonstrates that the arsenate is reduced to arsenite during the process. A fixed bed is able to reduce arsenate concentrations ranging from 120 to 1910 ppb to less than 10 ppb. The column adsorption behavior by the MGAC can well be described by a fixed-bed model.

1. Introduction

Arsenic pollution is a serious environmental problem due to its mobility and toxicity. More strict rules and regulations have been made to limit its discharge to sewers and water bodies. The U.S. Environmental Protection Agency (U.S. EPA) requires that public water systems must comply with the standard of 10 ppb for arsenic instead of the standard of 50 ppb used for years. This change leads to a great challenge to conventional physicochemical and biological technologies, such as membrane filtration, coagulation, oxidation, and phytoremediation.[1−6]

Adsorption has been considered as an effective technology. Activated alumina, activated carbon, iron oxide/hydroxide, and biomaterials are among the sorbents *employed* for removal of arsenic. They have distinctly different adsorption capacities, which are dependent on adsorbent dose, pH, contact time, initial arsenic concentration, and other solution conditions. For example, the maximum adsorption capacities of the algae *L. nigrescens* for arsenic are 45.2 (pH 2.5), 33.3 (pH 4.5), and 28.2 mg g^{-1} (pH 6.5),[7] while the maximum adsorption capacities are 8.5, 8.0, and 34.5 mg g^{-1} for a natural oxide consisting basically of Mn minerals and Fe oxides,[8] granular ferric hydroxide,[9] and a highly oxidized carbon,[10] respectively. On the other hand, the adsorption capacity of commercial activated carbons ranges from 1 to 4 mg g^{-1}. The low adsorption capacity precludes the commercial activated carbons from acting as a favorable adsorbent for arsenic adsorption according to several studies reported in the literature.[11,12]

In recent years, great effort has been directed to improve the efficiency and cost of adsorption technology for arsenic removal. The main technique is surface modification via iron oxide coating, such as iron-oxide-coated polymeric materials,[13] iron-oxide-coated sand,[14] iron-oxide-coated calcined bauxite,[6] and iron-oxide-impregnated activated alumina.[15]

Activated carbon has been widely used in the water industry because of its extended surface area, micro/mesoporous structure, and high adsorption capacity for organic substances such as humic acids (HAs). Commercial activated carbon has proved to have a low arsenic uptake capacity. Very limited studies have been reported on the improved adsorption of arsenic by activated carbon. It would be desirable to have activated carbon with enhanced arsenic adsorption.

Adsorption of inorganic contaminants onto activated carbons is mainly due to complexation with different surface oxygen-containing functional groups and/or electrostatic attractive interaction. Solution pH is known to be an important factor, and the optimum adsorption of arsenic is achieved at pH 5−6.[16] Modification of activated carbon for improved arsenic adsorption can be carried out by either impregnation of metal oxides or selective organic molecules. Iron oxide coating has been reported to enhance the adsorption capacity of activated carbon for As-(III) and As(V) by 1 and 2 orders of magnitude higher, respectively.[17,18]

In this study, a commercial activated carbon was modified via polyaniline impregnation for improving the adsorption of arsenate. Polyaniline was selected as it may lead to a change in the chemistry of activated carbon (e.g., surface charges). The adsorption properties, as a function of the operational conditions (e.g., solution pH, initial arsenic concentration, and competitive adsorbate), were determined. The simultaneous adsorption of arsenic and HA onto the modified carbon was studied. The adsorption mechanism was exploited by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy.

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2. Experimental Section

2.1. Materials and Equipment. Arsenic solutions were prepared for As(V) from sodium arsenate ($Na_2HAsO_4\cdot 7H_2O$) (Fluka AG, Switzerland). Humic acid (sodium salt), sodium chloride, hydrochloric acid, nitric acid, and sodium hydroxide, were obtained from Aldrich (Milwaukee, WI). The aniline and ethanol from Aldrich (Milwaukee, WI) and $FeCl_3\cdot 6H_2O$ from Nacalai Tesque Inc. (Kyoto, Japan) were used for carbon modification. All chemicals were of reagent grade.

The concentration of arsenic ions was measured using inductively coupled plasma-emission spectroscopy (*ICP-ES*) (Perkin-Elmer Optima 3000). Samples were acidified with concentrated HNO_3 and filtered with a 0.45-μm Whatman autovial syringeless filter (Clifton, NJ) before analysis. Solution pH was measured using an Accumet basic pH meter (Fisher Scientific). A total organic carbon (TOC) analyzer (5000A TOC Analyzer, Shimadzu, Japan) was used to determine the concentrations of organic substances.

2.2. Preparation of Raw Granular Activated Carbon. A granular activated carbon (GAC), Filtrasorb 200 from Calgon (Pittsburgh, PA), was ground and sieved to retain a fraction of the size in the range 500–850 μm. The resulting GAC was then washed with deionized (DI) water to remove the fine particles and dried at 110 °C in an oven for 5 h. It was cooled in a desiccator containing silica gel and stored in an airtight bottle, which is referred to as raw GAC (RGAC).

2.3. Preparation of Modified Granular Activated Carbon. A 0.05 g amount of aniline was made up to a 100 mL solution with ethanol. $FeCl_3\cdot 6H_2O$ and aniline with a molar ratio of 3:1 was then prepared. The $FeCl_3$ acted as a catalyst in the reaction. The solution was stirred for 3 h. Subsequently, 40-g of the RGAC was added to the solution; the resulting solution was stirred for 10 min. The entire mixture was vacuum filtered and thoroughly washed with the DI water to remove the excess reactants until the washed liquid became colorless. The carbon was dried at 110 °C in an oven for 5 h, cooled in a desiccator containing silica gel, and stored in an airtight bottle, which is referred to as MGAC. The chemical composition of the MGAC was determined by energy-dispersive spectroscopy (EDS) with a scanning electronic microscope (SEM) (JEOL, JSM-5600V, Japan). No iron was detected.

2.4. Characterization of Carbons. The specific surface areas of RGAC and MGAC were measured using the NOVA 3000 BET Analyzer (QuantaChrome). The samples were degassed overnight at 115 °C prior to analysis. The low-temperature nitrogen adsorption isotherms were then obtained and interpreted using the BET equation.

A potentiometric titration of RGAC and MGAC was performed by an autotitrator (716 DMS Titrino from Metrohm, Switzerland). A 0.5 g amount of carbon sample was added to a conical flask containing 100 mL of 0.05 M $NaNO_3$ solution, which was then placed in a shaker for 24 h. The titrants used were 0.1 N NaOH and 0.1 N HNO_3. The equilibrium time to establish surface charge was assumed to be 0.5 h.

The surface charge density (σ_o) of an activated carbon is defined by uptake of protons by the surface. It can be determined by the following equation,

$$\sigma_o = \frac{(c_A - c_B + [OH^-] - [H^+]) \times F}{S \times a} \tag{1}$$

where c_A and c_B are the concentrations of acid and base needed to reach a point on the titration curve in mol/L. $[H^+]$ and $[OH^-]$ are the concentrations of H^+ and OH^- in mol/L, F is the Faraday constant (96 490 C/mol), S is the specific surface area in m^2/kg, and a is the concentration of activated carbon in kg/L.

2.5. Instrumental Analysis. Fourier transform infrared spectroscopy was used to determine the vibration frequency changes in the functional groups in the activated carbons. The spectra were collected by an FTS-135 spectrometer (Bio-Rad) within the range of wavenumber of 400–4000 cm^{-1}. The specimens of RGAC and MGAC were first mixed with KBr and then ground in an agate mortar (Merck, for spectroscopy) at an approximate ratio of 1/100 for preparation of pellets (weight = 100 mg). The resulting mixture was pressed at 10 tons for 5 min. Sixteen scans and 8 cm^{-1} resolution were applied in recording the spectra. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra. All spectra were plotted using the same scale on the absorbance axis.

The XPS spectra of arsenic adsorbed onto the sorbent were obtained by a X-ray photoelectron spectrometer (Kratos Analytical, Ltd.) using monochromatized Al Kα radiation (1486.6 eV). Prior to XPS measurement all samples were dried for 2 h at 60 °C. The vacuum in the analysis chamber was always better than 5×10^{-8} Pa. Survey scans were collected from 0 to 1200 eV with a pass energy of 80 eV. High-resolution scans for the element As were performed over the 38–48 eV range, with the pass energy adjusted to 0.1 eV. Each spectral region was scanned between 15 and 200 times, depending on the intensity of the signal, to obtain an acceptable signal-to-noise ratio at reasonable acquisition times. Spectral deconvolution was performed using a curve-fitting program with subtraction of Shirley background; the line width (full width at half-maximum) of the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental compositions were determined from XPS peak area ratios after correction with the experimentally determined sensitivity factors.

2.6. Adsorption Kinetic Study. A 1.5 L volume of arsenic solution was prepared using DI water without pH control. The ionic strength of the solution was adjusted to 0.05 M using $NaClO_4$. A 7.5 gram amount of RGAC/MGAC was then added into the solution. The solution was stirred at a constant rate. Samples were taken at various time intervals and analyzed using ICP-ES. The experiments were conducted using different initial arsenic concentrations of 1.3 and 11.4 mg L^{-1}. The effect of the presence of 5 mg L^{-1} HA was also examined. The TOC analyzer was used to determine the concentration of HA.

2.7. Adsorption Equilibrium Study. In the pH-effect experiment a 0.5 g amount of RGAC/MGAC was added to each flask containing 100 mL of arsenic solution. The ionic strength of the solution was adjusted to 0.05 M using $NaClO_4$. The pH of the solution in each flask was adjusted by adding $HClO_4$ or NaOH. The flasks were placed in a shaking water bath with temperature being controlled at 25 °C for 48 h. The final pH of the solutions was measured. The final samples were analyzed using ICP-ES. The organic concentration due to modification was determined by the TOC analyzer.

In the adsorption isotherm experiment, different amounts of carbons were added into each flask containing 100 mL of a solution of fixed arsenate concentration. The pH of the solution was maintained at 5.5. Other experimental procedures are the same as the pH-effect experiment. The effect of the presence of HA of various concentrations was also examined.

2.8. Fixed-Bed Operation. In the fixed-bed experiments, arsenic solutions of various concentrations prepared using DI water without pH control were pumped through a flow rate meter into a MGAC column. The inner diameter of the column
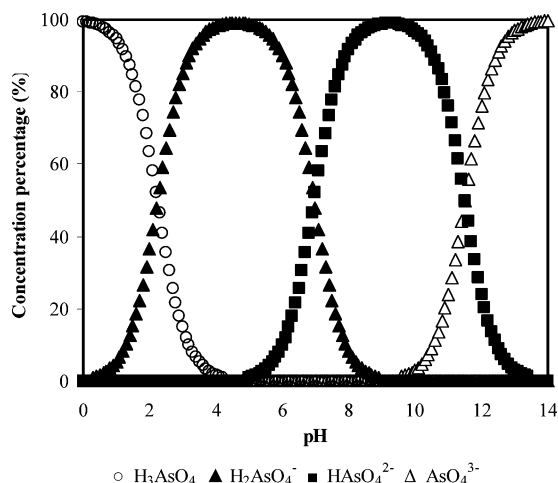
Figure 1. Distribution of arsenic(V) as a function of pH.

Figure 2. FTIR analysis of carbons.

Figure 3. Surface charge density of RGAC and MGAC by potentiometric titration.

was 1.0 cm, and the height of the filled MGAC was 25 cm; flow rates from 10 to 20 mL/min were maintained by a MICROPUMP gear pump (Cole-Parmer). The effluent samples were taken by an autosampler (730 Sample Changer, Metrohm, Switzerland), and the concentrations were subsequently analyzed using ICP-ES.

3. Results and Discussion

3.1. Distribution of Arsenic(V) Species. The distribution of As(V) species as a function of pH under an ionic strength of 0.05 M $NaClO_4$ at 25 °C was determined using MINEQL+.[19] It is seen from Figure 1 that H_3AsO_4 is the dominant species at pH < 2, $H_2AsO_4^-$ is the dominant species at pH between 2 and 7, $HAsO_4^{2-}$ is the dominant species at pH between 7 and 11.5, and AsO_4^{3-} is the dominant species at pH > 11.5. It indicates that the dominant As(V) species are negatively charged in natural water.

3.2. Determination of Specific Surface Areas. The specific surface area of the activated carbons before and after surface modification was 660 and 671 m^2 g^{-1}, respectively. This indicates that chemical modification does not result in any blockage of the porous structure of the activated carbon. This is consistent with our SEM observation of insignificant variation of carbon morphology after modification (figure not shown). This further illustrates that chemical modification would not change the organic adsorption performance of the activated carbon.

3.3. FTIR Study. Figure 2 shows the FTIR spectra of RGAC and MGAC. The spectrum of RGAC shows a wide and weak absorption band around 3700 cm^{-1}, which can be assigned to physically adsorbed water molecules. The split absorption bands at 1500−1600 cm^{-1} are suggested to be due to the overlapping of aromatic ring stretching vibrations with the bands of the carboxylate moieties.[20] Another weak peak around 1000 cm^{-1} may be attributed to the in-plane bending of aromatic C−H.

MGAC shows a continuously increasing IR absorption at higher wavenumbers, which can be attributed to absorption by the conjugated aromatic ring structures.[21] It may be due to the increased aromatic structure from the impregnated polyaniline. This is supported by the strong absorption peak at 625 cm^{-1} originating from aromatic C−H out-of-plane bending vibration. The strong and split peak at 2375 cm^{-1} can be assigned to the overlapping of stretching vibrations of carbon−oxygen groups due to ketones with the carbon−nitrogen groups. It might also
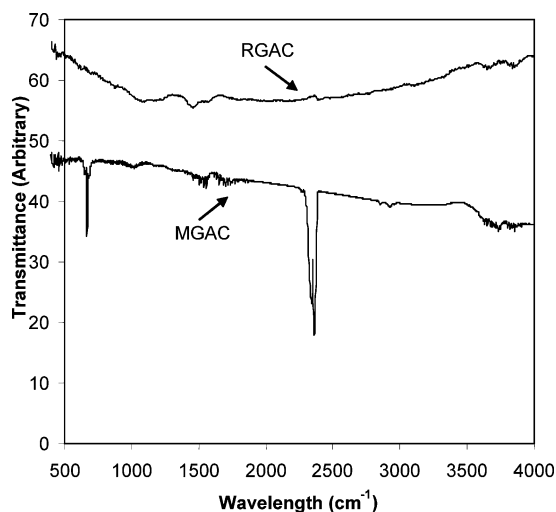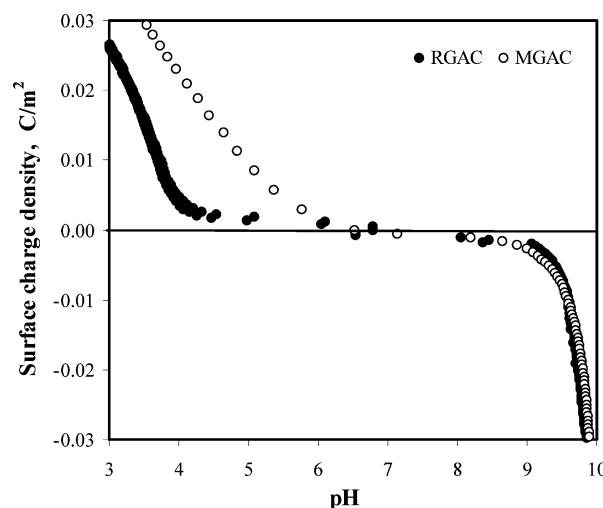
result from the conjugation of these functional groups with increased aromatic ring structures. This indicates that polyaniline modification brings about a distinct change of the surface functional groups of RGAC with an abundance of aromatic ring structures and nitrogen-containing functional groups.

3.4. Potentiometric Titration of Carbons. The potentiometric titration results of the RGAC and MGAC samples are shown in Figure 3. It can be seen that both samples are positively charged at acidic solution and negatively charged at basic solution. The point of zero charge (pH_{pzc}) values for the RGAC and MGAC are 7 and 6.5, respectively. The MGAC is found to contain much higher positive charges in acidic solution than the RGAC. However, both MGAC and RGAC show a similar amount of negative charges in alkaline solution.

Activated carbon has many functional groups as shown in the FTIR analysis and the references. Some of them are acid in nature, while some are basic.[22] These surface acid and base functional groups on the carbons are generally not coincident, and the distribution is complicated.[22] These surface functional groups are thus generalized as an apparent functional group (SOH). The following reactions involving protonation and deprotonation are suggested to take place at the carbon−liquid interfaces and account for the variation of the surface charge density in Figure 3

$$SOH + H^+ = SOH_2^+ \tag{2}$$

$$SOH = H^+ + SO^- \tag{3}$$
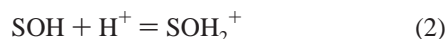
Equation 2 illustrates that the functional groups can be protonated in acidic solution, which renders the carbon positively charged. Equation 3 demonstrates that the functional groups can be deprotonated in basic solution, and the carbon becomes negatively charged. Comparison of MGAC with RGAC in Figure 3 reveals that eq 2 plays a more important role than eq 3. It indicates that the polyaniline modification introduces a large amount of proton-accepting functional groups on the surfaces of MGAC. These increased functional groups are likely the aromatic ring structures and nitrogen-containing functional groups, which is consistent with the FTIR study. Since both groups are electron rich with high proton affinity, MGAC has a larger proton capture capacity. Therefore, it renders the surface of modified activated carbon more positively charged in acidic solution. This implies that the modified activated carbon would have a higher affinity to anions, such as arsenate, due to electrostatic attractive interaction.

3.5. Adsorption Kinetics. Figure 4 shows the kinetics of arsenic removal by MGAC and RGAC at different initial As-(V) concentrations. It can be seen that the sorption process follows two phases. Rapid adsorption occurs initially, which is followed by a slower phase. The adsorption equilibrium can be established roughly at 2 h.

Humic acids, derived from the decay of various organisms, widely exist in natural surface and subsurface waters. Due to its large molecular size, HA may reduce adsorption kinetics through blockage of microporous structures of activated carbons, which results in high resistance of mass transfer in the micropores of carbons.[13] In order to find out the effect of humic acid on the adsorption kinetics, experiments were conducted with the result given in Figure 4. As shown, the presence of HA does not affect the As(V) adsorption kinetics. The insignificant effect of HA could be due to the small molecular size of As(V) and its low concentration levels.

A higher initial concentration of arsenate caused faster adsorption kinetics as demonstrated in Figure 4. This implicates that the kinetics of arsenate adsorption onto these activated carbons is mainly controlled by mass transfer of arsenate from the solution to the activated carbon surface, which is dependent on the arsenate concentration gradient between the solution and the activated carbon surface. Higher initial As(V) concentrations bring about a greater As(V) concentration gradient between the solution and the surface of the activated carbon, which eventually results in a higher adsorption rate.

Figure 5 shows the arsenic adsorption kinetics when an adsorbent dosage was 5 g L^{-1} and the initial As(V) concentration was 0.15 mg L^{-1} (150 ppb). The MGAC can reduce the As(V) to 0.0013 mg L^{-1} (1.3 ppb) in 30 min, while the RGAC only reaches an equilibrium As(V) concentration of 0.086 mg L^{-1} after 2 h. This clearly demonstrates that the MGAC is able to treat trace-level arsenic in the contaminated water below the current U.S. EPA standard. The improved adsorption performance of the MGAC for trace-level arsenic implicates that As-(V) is more affinitive to the MGAC surface.

Adsorption of arsenic onto activated carbons is reportedly achieved with a longer period. Manju et al. reported that complete removal of arsenic by coconut husk occurred after a contact time of 5 h.[11] Lorenzen et al. found that the adsorption equilibrium time of activated carbon was 24 h.[23] Comparison of the sorbent developed in this study with others shows that the sorbent is superior to most commercial sorbents.
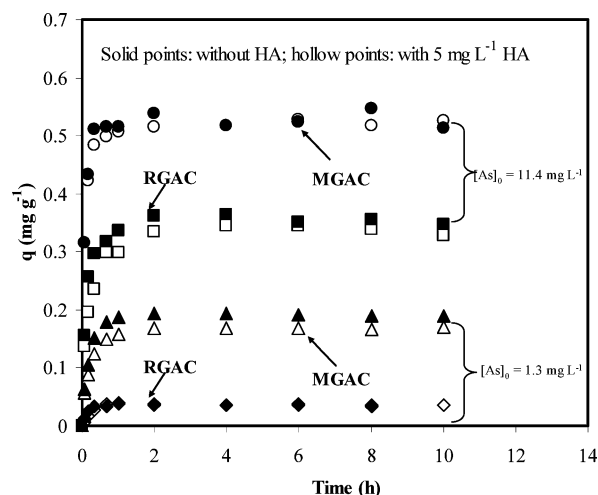

Figure 4. Kinetics of arsenate adsorption onto RGAC and MGAC at adsorbent dosage of 5 g L^{-1}.
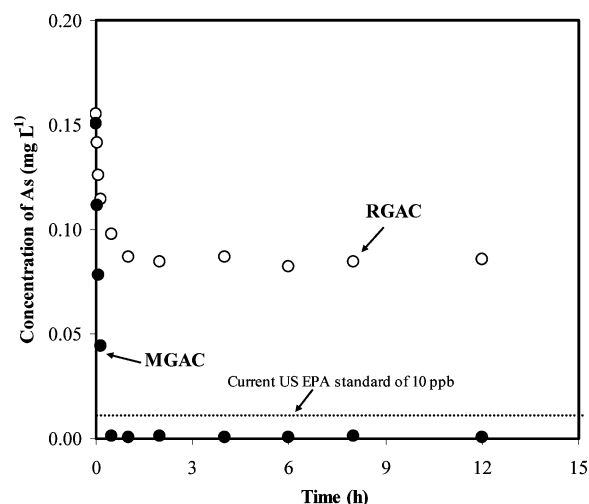

Figure 5. Comparison of arsenate adsorption kinetics on RGAC and MGAC at an initial arsenate concentration of 0.15 mg L^{-1} and adsorbent dosage of 5 g L^{-1}.
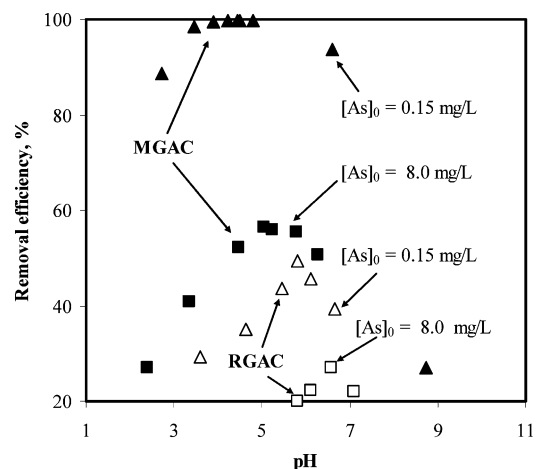

Figure 6. Variation of arsenate removal efficiency with pH for RGAC and MGAC at different initial arsenate concentrations of 8.0 mg L^{-1} (squares) and 0.15 mg L^{-1} (triangles).

3.6. Adsorption Equilibrium. 3.6.1. Effect of Solution pH. The pH effect on experimental results is given in Figure 6. It shows that optimum removal of arsenate occurs at a broad pH range for the MGAC and a sharply narrow pH for the RGAC. The optimum pH ranges for the MGAC at initial concentrations

of 0.15 and 8.0 mg L^{-1} are 3.0−6.8 and 4.0−6.6; those for the RGAC at the same initial concentrations are 6.0 and 6.5. Modification increases the optimum pH ranges, which covers the pH in natural water, such as groundwater. Thus, no pH adjustment is required when the MGAC is used in the treatment.

At the optimum pH, the MGAC can reduce trace-level arsenate concentrations as low as 150 μg L^{-1} to less than 1 μg L^{-1}. It was observed that the organic leaching of both MGAC and RGAC was less than 1.5 mg L^{-1} TOC in the solution pH ranging from 2 to 12 (data not shown). Loss of adsorbent and/ or modification agent, and secondary pollution can therefore be considered negligible. These observations demonstrate that the MGAC is particularly suitable for removal of trace-level arsenate contaminant at a wide pH range.

In the optimum pH range, the negatively charged species (H$_2$AsO$_4^-$) is dominant as shown in Figure 1. Arsenic may be adsorbed through surface complexion formation and/or electrostatic attractive interaction of H$_2$AsO$_4^-$ with the positively charged surface sites of activated carbons. Since the MGAC has many more positively charged surface sites than the RGAC, it exhibits a higher arsenic removal capacity. However, when the solution pH is far below the optimum pH range, neutral species (H$_3$AsO$_4$) increases, which reduces the electrostatic attractive interaction. On the other hand, when solution pH is far above the optimum values, the carbons become negatively charged, which reduces arsenate adsorption due to electrostatic repulsive interaction. Therefore, uptake of As(V) onto the carbons in the optimum pH range is favored owing to the positively charged surface and negatively charged H$_2$AsO$_4^-$ in acidic aqueous conditions, which can be illustrated as

$$S-OH_2^+ + H_2AsO_4^- = S-OH_2^+\text{-}H_2AsO_4^- \quad (4)$$
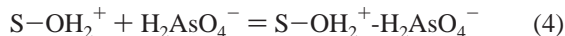
The existence of an optimum pH range suggests potential regeneration of the arsenic-containing carbons. It is expected that exposure of the carbons to an alkaline solution would lead to desorption of the arsenic for its recovery and reuse of carbon.

3.6.2. Adsorption Isotherm. The Langmuir adsorption model shown below was used to describe the isothermal arsenate adsorption

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (5)$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of adsorbate in solution (mg L^{-1}), q_{max} is the maximum adsorption capacity (mg g^{-1}), and b shows the affinity of the adsorbate to the adsorbent (L mg^{-1}).

Figure 7 shows the isothermal arsenate adsorption by the MGAC and RGAC at pH 5.5. It can be seen that the arsenate adsorption is well fitted by the Langmuir adsorption model with regression coefficients of determination (r^2) all above 0.99. This indicates a monolayer surface arsenate adsorption. It implies that the amount of surface functional groups in the carbon surface may be employed to determine its adsorption capacity as illustrated in eq 4. The best-fitted maximum adsorption capacities (q_{max}) of the RGAC and MGAC are 0.78 and 1.43 mg g^{-1}, respectively. These are quite consistent with the reported values in the literature.[23] Polyaniline modification of RGAC enhances the arsenate adsorption capacity by 84%. The corresponding affinity (b) values of the RGAC and MGAC are 0.17 and 0.50 L mg^{-1}, respectively, which confirms that As(V) is
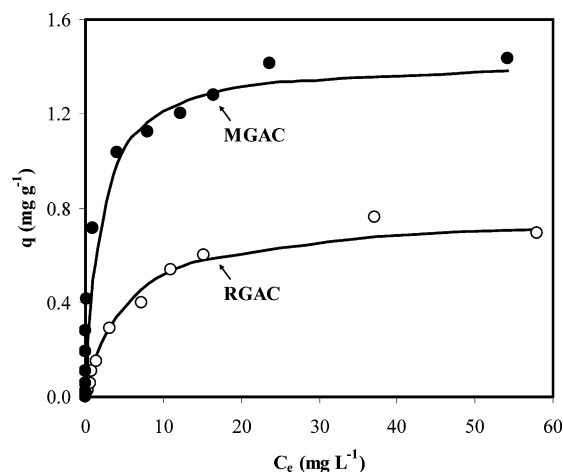

Figure 7. Langmuir adsorption model fitted arsenate adsorption isotherms of RGAC and MGAC at pH = 5.5.
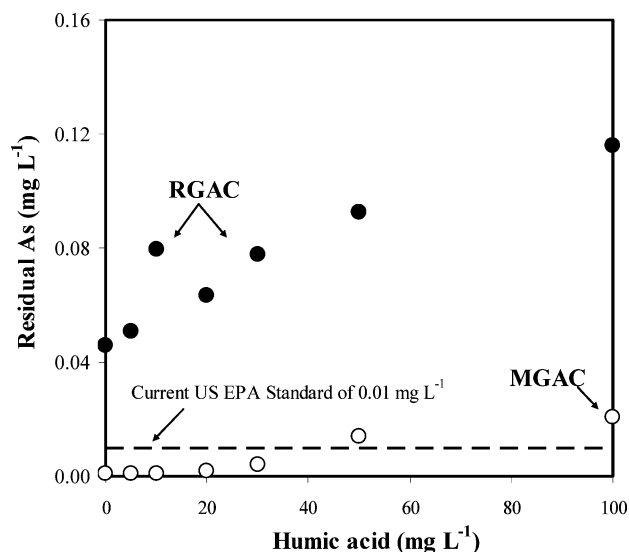

Figure 8. Effect of humic acid on arsenate adsorption onto RGAC and MGAC at pH = 5.5 at an initial arsenate concentration of 0.16 mg L^{-1}.

more affinitive to the MGAC surface. This further shows that the MGAC is more favorable for As(V) removal than the RGAC.

3.6.3. Effect of Humic Acid. The presence of humic acid may affect the adsorption capacity of arsenate due to its competition for surface adsorption sites of activated carbons. Figure 8 demonstrates the negative influence from the humic acid on the adsorption performance of RGAC and MGAC. A similar observation can be found in Figure 4. With an increase in the HA concentration, the negative influence from the humic acid becomes more obvious. In the absence of HA, the residual concentrations are 0.046 and 0.001 mg L^{-1} for the RGAC and MGAC, respectively. However, the concentrations increase to 0.116 and 0.021 mg L^{-1} for the RGAC and MGAC, respectively, when the HA concentration is 100 mg L^{-1}. Nevertheless, the MGAC still outperforms the RGAC; the residual concentration of MGAC in most cases is below the U.S. EPA standard of 10 ppb.

HA adsorption is highly pH dependent; it decreases with an increase of solution pH.[24] At pH 5.5 in the experiment (Figure 8) the HA is negatively charged. In the same pH range the dominant arsenate species are also negatively charged as shown in Figure 1. The activated carbons at that pH carry positive charges (Figure 3). Competition between the HA and arsenate
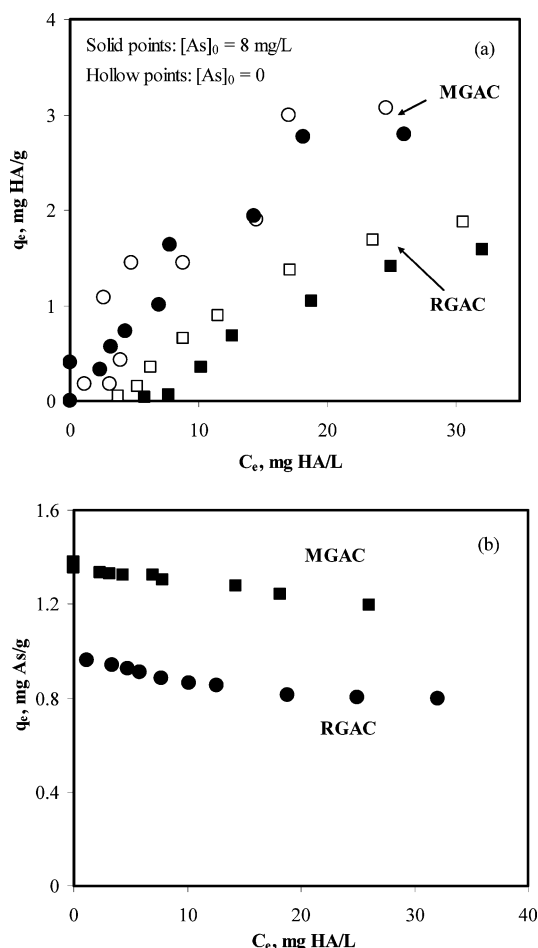
Figure 10. Performance of fixed-bed column for arsenate adsorption by MGAC.

Figure 9. Simultaneous adsorption of humic acid and arsenate: (a) HA and (b) As(V). Carbons = 5 g L^{-1}, [As]$_0$ = 8 mg L^{-1}, contact time = 24 h.

species for the positively charged activated carbons thus occurs, leading to lower adsorption of As(V).

3.6.4. Simultaneous Adsorption of Humic Acid and Arsenate. Most activated carbons have an excellent adsorption capacity for organic substances such as humic acid; however, they are less effective in removal of arsenic. The chemical modification approach in this study aims at enhancement of arsenic removal on activated carbons. It is desirable that the excellent organic adsorption of the carbons can still be maintained.

Figure 9 demonstrates the simultaneous adsorption of humic acid and arsenate. The presence of arsenate slightly reduces the HA adsorption. It is encouraging to note that the chemical modification approach enhances the organic adsorption capacity of activated carbon by almost 100%. The adsorption capacity of the modified carbon is lower than some other adsorbents such as Fe(III)-doped alginate gels and modified biomass.[25,26] However, activated carbon surpasses those sorbents as it is able to simultaneously remove organic substances and arsenic from aqueous solutions.

The MGAC can obtain higher simultaneous adsorption of both arsenate and humic acid. This is due to the fact that chemical modification does not greatly alter the physical properties of the activated carbons (e.g., specific surface area discussed early), leading to maintenance of its organic compound adsorption advantage. Chemical modification introduced beneficial functional groups for arsenate adsorption. Therefore, the modified activated carbon is good for both arsenate and organic pollutants removal from multiple-polluted wastewaters.
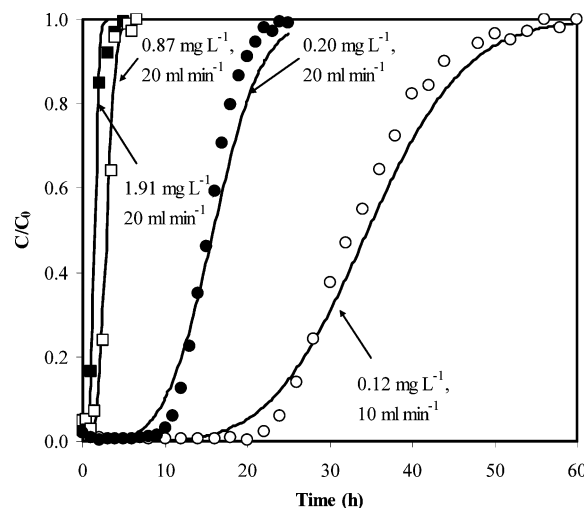
3.7. Fixed-Bed Operation and Modeling. A fixed-bed reactor is widely used in adsorption of both organic contaminants and heavy metal ions. Its advantages include stable performance and ease in operation. Figure 10 shows the breakthrough curves of an MGAC adsorption column. The performance depends on both chemical and physical properties in the solid and liquid phases such as the influent arsenate concentration and volumetric flow rate of solution. Higher influent concentration and flow rate would cause earlier breakthrough.

The breakthrough time is an important parameter in evaluation of fixed-bed reactor design and operation. In order to easily compare operational performances of columns, the number of bed volumes (BV) is used.[27] It can be determined from Figure 10 that the breakthrough time is 658 BV when the influent As-(V) concentration is 0.12 mg L^{-1}.

It has been reported that external mass transfer and pore diffusion control metal sorption kinetics. A fixed-bed model with consideration of external mass transfer, pore diffusion, advection, and longitudinal dispersion was used to describe the sorption behavior in the carbon columns.[28] The following control equation can be used to describe the adsorption in the fixed bed column

$$\frac{\partial C_b}{\partial t} + v\frac{\partial C_b}{\partial z} - D_L\frac{\partial^2 C_b}{\partial z^2} + \frac{1-\epsilon_b}{\epsilon_b}\frac{d(\epsilon_p\bar{c} + \rho_p\bar{q})}{dt} = 0 \quad (6)$$

where the term d($\epsilon_p\bar{c} + \rho_p\bar{q}$)/d$t$ represents the overall rate of sorption kinetics for metal averaged over a particle. C_b is the bulk concentration, kg m^{-3}, $\bar{c}$ is the averaged concentration within the particle pore, kg m^{-3}, D_L is the longitudinal dispersion coefficient, m^2 s^{-1}, $\bar{q}$ is the averaged concentration in the solid phase, kg kg^{-1}, t is time, s, v is the interstitial velocity of the bulk flow, m s^{-1}, and z is the axial distance from the column entrance, m. ϵ_p is the porosity of the particle, ϵ_b is the fixed bed porosity, and ρ_p is the particle density, kg m^{-3}.

A modified orthogonal collocation method was used to solve the model. Seven radial collocation points for the particle and 10 axial collocation points were used in the simulation. The partial differential equations were replaced by 10 × 8 ordinary differential equations (ODE), which were subsequently solved by an ODE solver, EPISODE.[29] The kinetic parameters were obtained by the best-fitting approach.

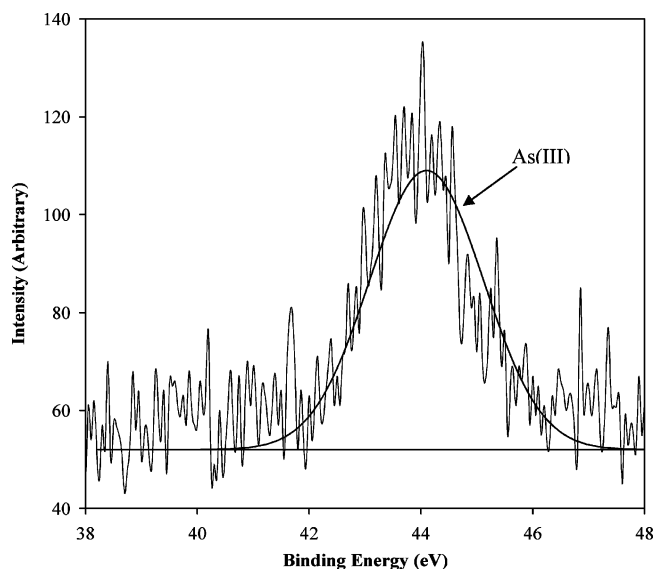The equilibrium relationship required in the model was described by the Langmuir isotherm. The simulation results of

Figure 11. XPS analysis of As-loaded MGAC.

the fixed-bed model are plotted together with the experimental data in Figure 10 with the external mass transfer coefficient and the internal diffusivity fixed at 2.5×10^{-5} and 1.0×10^{-9} $m^2 \, s^{-1}$, respectively, for the four influent concentrations studied. The model describes the adsorption performance in the fixed-bed column well. The model parameters are of the same magnitude as those published.[27] The modeling results confirm that the sorption behavior is dependent on the dual-resistant mass transport (i.e., external mass transfer and pore diffusion), advection (due to the solution flowing through the carbon columns), and dispersion. From a practical application standpoint, the fixed-bed model is applicable in the design of fixed-bed columns for treatment of the contaminants.

3.8. XPS Analysis. The oxidation states of arsenic adsorbed in the activated carbon surface were determined with XPS since different arsenic species have characteristic binding energies (BEs). The BEs for As(V) in Na_2HAsO_4, As(III) in $NaAsO_2$, and As(0) are 45.5, 44.2, and 41.5 eV, respectively.[30]

The XPS spectrum of arsenic adsorbed in the MGAC surface is shown in Figure 11. A single As 3d photoelectron peak occurs at 44.1 eV corresponding to the characteristic peak position of As(III). No obvious As(V) and As(0) peaks are detectable. It is evident that As(V) is reduced when adsorbed by the MGAC according to eq 4 discussed early. As indicated by the FTIR spectra, the MGAC contains increased electron-rich aromatic ring structures and nitrogen-containing functional groups. These structures and functional groups act as electron donors for the reduction of As(V) to As(III). Though As(III) is more toxic than As(V) in aqueous solution, the strong affinity of arsenic to the MGAC surface implicates that secondary pollution from it would be negligible, especially when the MGAC is used for adsorption of trace-level arsenate.

4. Conclusions

Polyaniline modification results in anabundance of electron-rich aromatic ring structures and nitrogen-containing functional groups, which are favorable for arsenate adsorption. It does not affect the specific surface area of activated carbon while enhancing the positive surface charge in the solution pH ranging from 3 to 6. The maximum arsenate adsorption capacity is increased by about 100%. The modification broadens the optimal pH range for arsenate adsorption: pH of 3.0−6.8 and 4−6.6 for the MGAC at initial arsenic concentrations of 0.15 and 8.0

mg L^{-1} vs pH 6.0 and 6.5 for the RGAC at the same concentrations. The MGAC demonstrates greater performance for simultaneous adsorption for both arsenate and humic acid.

The excellent adsorption performance of modified activated carbon for possible arsenate wastewater treatment is further illustrated by a continuously operated fixed-bed reactor. The carbon is able to reduce the arsenate concentrations ranging from 120 to 1910 ppb to less than 10 ppb. The column adsorption behavior by MGAC is well described by a fixed-bed model, which provides useful information for designing pilot- and full-scale columns for water and wastewater treatment facilities.

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