Perchlorate adsorption and desorption on activated carbon and anion exchange resin

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ABSTRACT

The mechanisms of perchlorate adsorption on activated carbon (AC) and anion exchange resin (SR-7 resin) were investigated using Raman, FTIR, and zeta potential analyses. Batch adsorption and desorption results demonstrated that the adsorption of perchlorate by AC and SR-7 resin was reversible. The reversibility of perchlorate adsorption by the resin was also proved by column regeneration test. Solution pH significantly affected perchlorate adsorption and the zeta potential of AC, while it did not influence perchlorate adsorption and the zeta potential of resin. Zeta potential measurements showed that perchlorate was adsorbed on the negatively charged AC surface. Raman spectra indicated the adsorption resulted in an obvious position shift of the perchlorate peak, suggesting that perchlorate was associated with functional groups on AC at neutral pH through interactions stronger than electrostatic interaction. The adsorbed perchlorate on the resin exhibited a Raman peak at similar position as the aqueous perchlorate, indicating that perchlorate was adsorbed on the resin through electrostatic attraction between the anion and positively charged surface sites.

1. Introduction

Perchlorate (ClO_4^-) is an alarming contaminant in groundwater and surface water which may contaminate more than 12 million people's drinking water sources in the United States [1–3]. The USEPA reported that perchlorate products were manufactured and processed in approximately 40 states, and the release of perchlorate to groundwater and surface water was observed in more than 20 states [4]. The major sources of perchlorate were from historical disposal practices of rocket fuel and explosives by the aerospace and chemical industries [5]. Naturally occurring perchlorate is also found in the hyperarid Atacama Desert, in Chilean nitrates and their derived nitrate fertilizer, and in southeastern California caliche nitrate deposits [6,7].

Perchlorate is a health concern because it can block the uptake of iodine in the thyroid gland, affecting the production of thyroid hormones and possibly causing mental retardation in fetuses and infants [8]. The USEPA adopted a new drinking water standard of 24.5 μg/L for perchlorate in 2005. The State of Massachusetts issued a clean-up standard of 2 μg/L for perchlorate in 2006 and the Office of Environmental Health Hazard Assessment (OEHHA) of California set a Public Health Goal of 6 μg/L.

Because perchlorate ions are nonvolatile, highly soluble, and kinetically inert in water, it is very difficult to remove perchlorate from water effectively [2,9]. Various treatment technologies have been studied for perchlorate removal from water. Biological treatment is cost-effective for water contaminated with high perchlorate concentration and poor water quality (high organics and suspended solids) [2,10–12]. However, biological processes can be costly for the treatment of large-volume perchlorate-containing waters having low perchlorate concentration because a highly reducing environment is needed to reduce perchlorate. Furthermore, additional treatment processes are required to remove added nutrients and potential pathogens [2,10].

Activated carbon (AC) is a common sorbent used to remove organic contaminants from water. AC media are generally considered cost-effective for water treatment when used for removal of non-polar contaminants with low water solubility [13,14]. The

spent AC can also be thermally reactivated, allowing it to be reused at a cost less than replacing the AC with new sorbent. AC was not found to be effective for perchlorate removal [15] because perchlorate exists in anionic species [16]. Therefore, some modified AC sorbents, such as iron-preloaded, ammonium-tailored, and cationic surfactant-treated, were used to remove perchlorate [15,17,18]. In rapid small-scale column tests (RSSCT), cationic surfactant-tailored AC had 30 times higher perchlorate capacity than unmodified AC [18].

Ion-exchange technology is widely used for water treatment due to its simplicity, high capacity, and capability of operating at a relatively high flow rate with a small treatment unit [2,9,19]. Anion exchange resins used for perchlorate treatment can be divided into two types. One type is selective but non-regenerable strong-base anion (SBA) exchange and another is non-selective or low-selective resins which are regenerable with NaCl solution [19]. The bifunctional-anion exchange resin (Purolite A-530E) is very effective for perchlorate removal [20,21]. The bifunctional resin is composed of two quaternary ammonium groups: a long alkyl chain for higher selectivity, and a shorter alkyl chain for improved reaction kinetics [19,21]. The greatest challenge associated with using ion-exchange technology is regeneration of spent resins since perchlorate on most anion exchange resins is difficult to displace with chloride [20,21]. Although $FeCl_3$–HCl solution can be used to release perchlorate from spent resins, high concentration $FeCl_3$–HCl solution is hazardous and the spent solution must be treated [21,22]. In this study, SR-7 resin was selected for perchlorate adsorption and desorption because it is a commonly used anion exchange resin for treatment of perchlorate contaminated water.

Although a large amount of research has been dedicated to perchlorate treatment, the reversibility of perchlorate adsorption and kinetics of perchlorate release have not been sufficiently investigated. In this research, perchlorate adsorption and desorption kinetics and isotherms on AC and SR-7 resin were systematically investigated. The mechanisms of perchlorate adsorption were studied using Zeta potential measurements, Raman, and FTIR analyses. The information obtained from the work will be important for designing efficient spent adsorbent treatment processes.

2. Materials and methods

2.1. Materials

All stock solutions were prepared using ACS grade chemicals and deionized water (DI). Stock solutions of perchlorate were prepared by dissolving solid $NaClO_4 \cdot H_2O$ (Fisher Scientific, Springfield, NJ, USA) in DI water. The AC (GAM 025, particle size = 0.185–0.381 mm) and SR-7 resin were received from Nichem Company (Irvington, NJ, USA) and Sybron Chemicals Inc. (Birmingham, NJ, USA), respectively. The SR-7 resin is a strong-base anion exchanger with a macroporous polystyrenic matrix and quaternary amine functional groups.

2.2. Perchlorate adsorption and desorption tests

The adsorption and desorption kinetics of perchlorate on AC and SR-7 resin were tested by mixing 0.5 g of each adsorbent with 25 mL of solution containing 10 mg/L perchlorate and 0.5% NaCl (Fisher Scientific, Springfield, NJ, USA). Samples in capped test tubes were shaken at the speed of 130 rpm in an Environmental Incubator Shaker (Model G24, New Brunswick Scientific Co., Edison, NJ, USA) based on the preliminary test for perchlorate sorption and desorption. At specified time intervals of 5, 10, 15, 30, and 120 min, an aliquot of sample was taken and analyzed for the concentration of perchlorate remaining in the supernatant solution.

For most of the resins studied, a 24-h equilibrium time was found to be sufficient for adsorption and desorption to reach equilibrium.

Perchlorate adsorption and desorption isotherms were determined by equilibrating AC and SR-7 resin for 24 h at a mixing speed of 130 rpm. In the batch equilibrium experiments, 0.5 g AC and SR-7 resin were added to a set of 25 mL 0.5% NaCl solutions containing 5, 15, 30, 40, 50, and 60 mg/L of perchlorate for AC, and containing 3, 10, 30, 50, 100, 150, 300, 500, 700, and 900 mg/L of perchlorate for SR-7 resin, respectively, at an initial pH of 7.0. The pH of the solution was controlled at 7.0 ± 0.5 through intermittent pH adjustment using 0.1N HCl and NaOH. After 24 h, the supernatant was centrifuged using an Eppendorf Centrifuge (Brinkmann Instruments, Inc., Westbury, NY, USA) at 10,000 rpm for 10 min. After the adsorption kinetic and isotherm experiments, the desorption of perchlorate was studied using the perchlorate-loaded adsorbents. Briefly, the clear supernatant solution was carefully removed from the adsorption container using a pipette and then replaced with 25 mL of 0.5% NaCl solution. The samples were mixed for 24 h for release of perchlorate from the resin and the perchlorate concentrations in the centrifuged supernatant were analyzed.

The effect of NaCl concentration on perchlorate adsorption was evaluated by mixing 1.0 g AC and 0.5 g SR-7 resin with 25 mL of solution containing the desired NaCl concentration (0%, 0.1%, 1%, 10%, or 15% NaCl), and 600 and 2000 mg/L perchlorate, respectively. The pH of the solutions was controlled at 7.0 ± 0.5 with HCl and NaOH. The solution was mixed for 3 h and then was centrifuged for the analysis of soluble perchlorate.

2.3. Column regeneration of spent SR-7 resin

Column experiments were performed only on SR-7 resin to evaluate perchlorate desorption from spent SR-7 resin, because the perchlorate adsorption on SR-7 resin was higher than that on AC. The spent perchlorate-saturated resin was prepared by mixing 10 mL SR-7 resin (6.75 g) with 500 mL of 200 mg/L perchlorate solution for 24 h. The perchlorate-loaded resin was wet-packed into a glass column and rinsed with 10 mL of DI water to remove the residual perchlorate solution. The perchlorate elution test was conducted by passing NaCl solutions through the resin column at different flow rates. The effluent samples were collected at different times for perchlorate analysis. All effluent was collected into a container for measurement of cumulative volumes of effluent and average perchlorate concentration, and for the calculation of perchlorate recovery from the spent resin.

2.4. Perchlorate analysis

Perchlorate concentration was determined using two Dionex ion-exchange chromatography (IC) systems (Dionex, Sunnyvale, CA). The first one was equipped with a 25 μL sample loop, a set of 4×250 mm AS16 and AG16 columns, a 4-mm ASRS Ultra II suppressor, and an electrical conductivity detector. The suppressor current was 100 mA. The eluent was set to 40 mM KOH. The sample running time was 20 min. With this setup, the detection limit for perchlorate was 100 μg/L. The other one was equipped with an EG40 eluent generator, a 100 μL sample loop, a set of 2×250 mm AS16 and AG16 columns, a 2-mm ASRS Ultra II suppressor, an electrical conductivity detector. The suppressor current was 100 mA. The eluent was set to 20 mM KOH. The injection volume was 100 μL. The sample running time was 25 min. With this setup, the detection limits for perchlorate was 4 μg/L.

2.5. Zeta potential measurements

The zeta potential of clean and perchlorate-loaded adsorbents was measured at different equilibrium pH using a Nano ZS Zetasizer (Malvern Instruments Limited, Malvern Worces, UK). The clean adsorbent samples were prepared in 25 mL suspensions containing 0.2% NaCl and 0.1 g AC or SR-7 resin. The initial pH of the suspensions was adjusted between 2 and 10 and they were mixed for 24 h. Then, the zeta potential of the adsorbent and final pH of the suspension was measured. The perchlorate-loaded adsorbent samples were prepared with the same procedures, except that the suspensions contained 60 and 400 mg/L perchlorate for AC and resin systems, respectively. After mixing, the amount of perchlorate adsorbed on the solids was also determined in addition to the measurement of zeta potential and pH. In another set of experiments, 25 mL suspensions containing 0.1 g SR-7 resin, 0.2% NaCl, and 0, 100, 200, 300, and 400 mg/L perchlorate were mixed for 24 h. The pH of the suspensions was controlled at 7.0 ± 0.5. The final pH, amount of perchlorate adsorbed, and zeta potential of the resin in the suspensions were measured.

2.6. FTIR analysis of activated carbon

The AC samples were prepared by mixing the adsorbent with solutions containing 0, 100, 1000, and 10,000 mg/L perchlorate. The standard materials of sodium perchlorate (solid form) and 10% sodium perchlorate solution (liquid form) were also analyzed. Infrared absorption spectra were recorded from pressed discs of mixtures of the AC samples and KBr in the range of 4000–700 cm^{-1}, averaging the data of 50 successive scans. The surface functional groups of AC and adsorbed perchlorate were characterized using FTIR (FT-IR 4000, JASCO Inc., Japan). Measured spectra were baseline-corrected and smoothed according to the Savitzky–Golay method [23] by means of a 25-point smoothing filter. For spectral characterization, absorption peaks were compared with literature data.

2.7. Raman spectroscopy analysis

Raman spectroscopic analysis was performed to provide insights into the mechanisms of perchlorate interactions with AC and SR-7 resin. In the Raman analysis, 0.5 g AC and SR-7 resin were placed in 50 mL of aqueous solutions containing perchlorate concentrations of 500 and 2000 mg/L, respectively. The AC and SR-7 resin samples were allowed to mix in the solution for 24 h. The wet solid samples were analyzed by Raman spectroscopy (Nicolet Almega XR Dispersive Raman, Thermo Electron Corporation, USA). The laser wavelength used in Raman measurement was 780 nm. The measurement conditions were collect exposure time 10 s and sample exposure three times. The maximum resolution of the spectrometer was ca. 4 cm^{-1}. The standard materials sodium perchlorate (solid form) and 10% sodium perchlorate solution (liquid form) were also analyzed. The solid and solution samples were prepared with the Premium Microscope Slides (Fisher Scientific).

3. Results and discussion

3.1. Batch adsorption and desorption of perchlorate

Kinetic results of perchlorate adsorption and desorption on AC and SR-7 resin are presented in Fig. 1a and b. The initial perchlorate concentration in the adsorption tests was 10 mg/L. Perchlorate removal by AC and resin reached equilibrium within 30 min. Perchlorate was completely removed by the resin, whereas approximately 85% of the perchlorate was removed by AC.
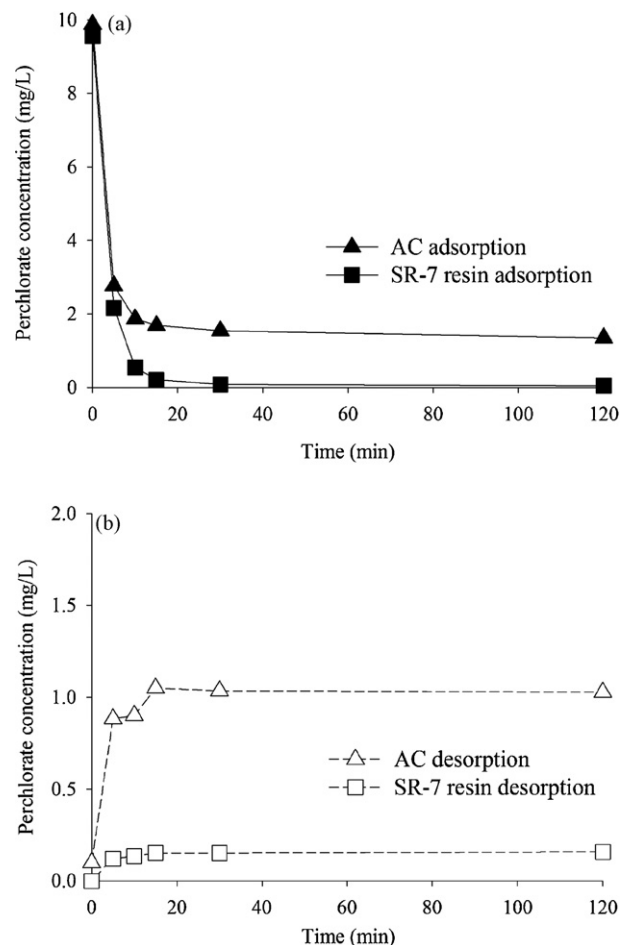

Fig. 1. Kinetics of perchlorate (a) adsorption and (b) desorption by AC and SR-7 resin. Adsorbent = 0.5 g; solution = 25 mL, initial perchlorate = 10 mg/L; 0.5% NaCl; pH 7.0 ± 0.5.

When the perchlorate-loaded adsorbents were mixed with 0.5% of NaCl solution, perchlorate desorption occurred rapidly and reached equilibrium within 30 min (Fig. 1b). The equilibrium perchlorate concentration was about 0.1 and 1.0 mg/L for the resin and AC, respectively, though there was more adsorbed perchlorate on the resin than on AC. About 12.2% and 1.6% of adsorbed perchlorate were released from AC and resin, respectively. The results indicated that both adsorption and desorption of perchlorate on AC and resin took place rapidly and the resin had much higher affinity for perchlorate than AC did.

The adsorption isotherms of perchlorate were determined over a wide range of initial perchlorate concentrations, from 5 to 60 mg/L for AC and from 3 to 900 mg/L for SR-7 resin, at pH 7.0 ± 0.5. Fig. 2 shows the adsorption and desorption isotherms of perchlorate by AC and SR-7 resin. To compare the adsorption capacities of perchlorate, the classical single component Freundlich model was used to simulate the experimental data.

$$\theta = KX^{\nu} \tag{1}$$

where K is the Freundlich capacity coefficient ((mg g^{-1})/(mg L^{-1})), ν is the Freundlich exponent reflecting the site energy distribution and adsorption intensity, θ is the solid-phase concentration (mg/g), and X is the equilibrium aqueous-phase concentration (mg/L). The dashed lines in Fig. 2 are Freundlich fitting curves.

The best-fit values of K and ν for AC were 0.51 ((mg g^{-1})/(mg L^{-1})) and 0.65, and those for SR-7 resin were
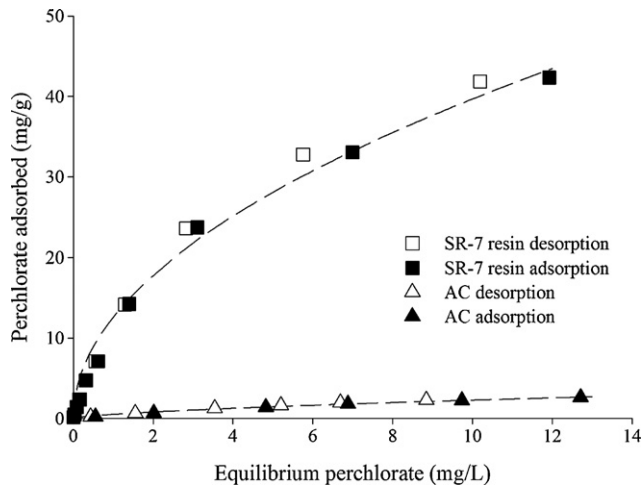
Fig. 2. Adsorption and desorption isotherm of perchlorate by AC and SR-7 resin. Adsorbent = 0.5 g; solution = 25 mL, 0.5% NaCl; pH 7.0 ± 0.5. The lines are best fitting curves calculated using the Freundlich equation.
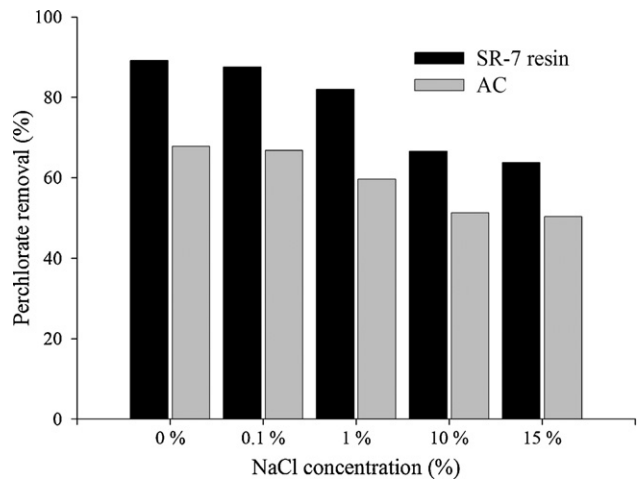

Fig. 3. Effect of NaCl on perchlorate removal by AC and SR-7 resin, AC system: initial perchlorate = 600 mg/L; AC content = 1.0 g; SR-7 resin system: initial perchlorate = 2000 mg/L; SR-7 resin content = 0.5 g; solution = 25 mL; equilibrium pH 7.0 ± 0.5.

12.6 $((mg\,g^{-1})/(mg\,L^{-1}))$ and 0.5, respectively. Xiong et al. [20] tested perchlorate removal by IRA-900 resin (a standard Type I SBA resin) and obtained the K value of 25 $((mg\,g^{-1})/(mg\,L^{-1}))$. The smaller K value for SR-7 resin than for IRA-900 resin can be mainly attributed to the 0.5% NaCl solution used in this study. Both resins have quaternary amine functional groups and a polystyrene matrix. The polystyrene matrix (hydrophobic nature) has higher perchlorate selectivity than the polyacrylic matrix (hydrophilic nature) [20].

The reversibility of perchlorate adsorption was assessed by comparing the adsorption and desorption isotherms. After adsorption experiments, the supernatants were decanted and then replaced with 0.5% NaCl solution to test the desorption isotherm. The results in Fig. 2 showed that the adsorption and desorption isotherms essentially overlapped, indicating that the perchlorate adsorptions by AC and SR-7 resin were reversible phenomena. This result suggest that, thermodynamically, all adsorbed perchlorate on the AC and SR-7 resin can be released into a 0.5% NaCl solution provided enough solution was used.

The effect of NaCl concentration on the removal of perchlorate by the SR-7 resin and AC is illustrated in Fig. 3. Perchlorate removal decreased gradually with increasing salt concentration. However, 60% and 50% of perchlorate was adsorbed by SR-7 resin and AC, respectively, even at 15% NaCl. Perchlorate anions are selectively and strongly sorbed as a result of their low hydration energy and large size [21]. The increasing order of affinity of singly charged ions for strong-base anion-exchange resins is well known: bicarbonate < chloride < nitrate < perchlorate [21].

3.2. Column desorption of perchlorate from spent resin

Fig. 4 shows effluent perchlorate concentration as a function of effluent bed volumes with different NaCl concentrations and flow rate. Perchlorate recovery in the figure was calculated based on the total amount of perchlorate on the resin and cumulative perchlorate in the effluent. During the initial 230 bed volumes of the column test, 0.5% NaCl solution was pumped through the resin column at a flow rate of 0.2 mL/min. The empty bed contact time (EBCT = bed volume/flow rate) was 50 min and the retention time (RT = pore volume/flow rate) was 16 min. The relatively long retention time and rapid desorption kinetics shown in Fig. 1 favored release of perchlorate from the resin. Effluent perchlorate concentration increased to about 1500 µg/L during the initial elution period. The flow rate

was 1.0 mL/min between bed volumes of 230–1500 and was further increased to 5.0 mL/min (EBCT = 2 min) between bed volumes of 1500–5750. During this period, the effluent perchlorate concentration decreased to about 560 µg/L, and the cumulative perchlorate release was about 73%. The low recovery of the perchlorate by large bed volumes of solution was due to the low NaCl concentration and short EBCT.

When the NaCl concentration was increased to 5.0% at 5750 bed volumes, the effluent perchlorate concentration increased to 1800 µg/L. Then, it decreased dramatically to approximately 100 µg/L while nearly all perchlorate on the resin was released. The slightly greater than 100% perchlorate recovery measured could be attributed to overall analytical and experimental errors. The results demonstrated that all perchlorate on the resin could be released by large amounts of relatively low NaCl solution. This is consistent with the reversible adsorption behavior observed in Fig. 2. According to Fig. 3, the amount of solution used for regeneration of the resin could be reduced if a high NaCl concentration was used. However, the amount of concentrated brine solution needed for complete regeneration of the resin could be prohibitively large due to the high selectivity of the resin for perchlorate. In addition, the perchlorate in the spent brine solution
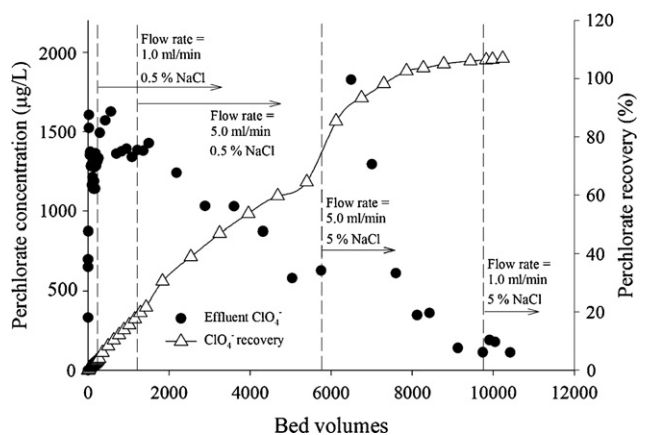

Fig. 4. Column leaching of perchlorate from spent SR-7 resin, resin volume in column = 10 mL, regeneration solution = 0.5 and 5% NaCl, flow rate = 0.1, 1.0, and 5.0 mL/min.
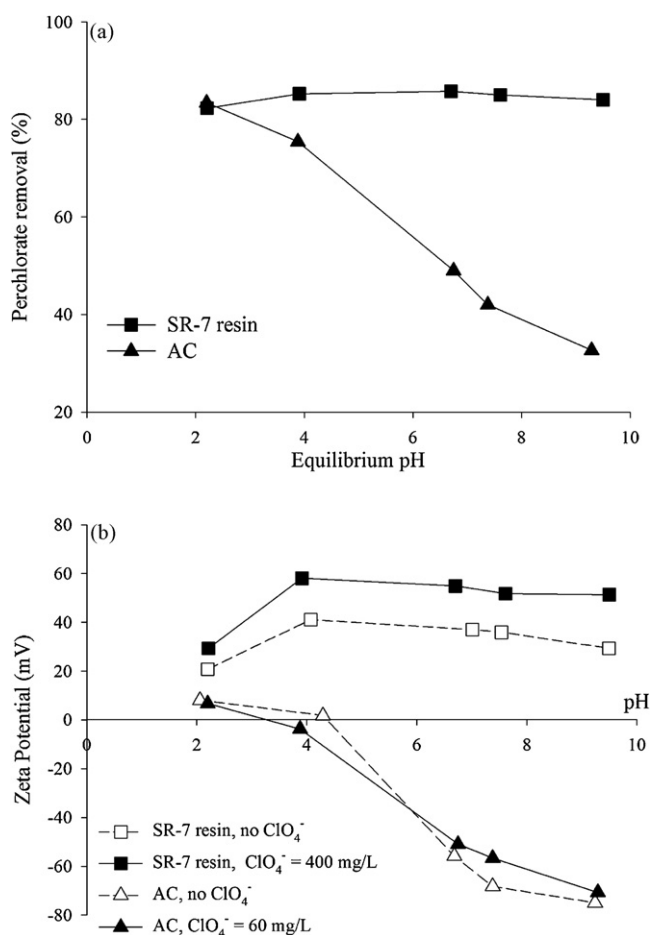
Fig. 5. (a) Effect of pH on perchlorate removal by AC and SR-7 resin. AC system: initial perchlorate = 60 mg/L; AC content = 4 g/L; SR-7 resin system: initial perchlorate = 400 mg/L; SR-7 resin content = 4 g/L; solution = 25 mL containing 0.2% NaCl. (b) Zeta potential of AC and SR-7 resin as a function of pH in 0.2% NaCl solution with and without perchlorate.

with high salt content cannot be treated with biological reduction processes.

It is known that perchlorate-loaded polystyrene resin such as SR-7 resin is more difficult to regenerate than polyacrylic resins. Batista et al. [24] reported that 96% of the perchlorate was recovered for an acrylic SBA resin with 13 bed volumes of 12% NaCl solution, compared to only 17% perchlorate release for a styrenic SBA resin. Tripp and Clifford [25] compared the regeneration efficiency of perchlorate-saturated polyacrylic and polystyrene resins using 1N NaCl solution. The polyacrylic resin required 9 equiv. of Cl/(equiv. of resin) (40 lb/ft^3) to achieve 90% elution of perchlorate, while it would require more than 17 times as much regenerant to achieve the same perchlorate elution for a polystyrene-based resin.

3.3. The effect of pH and zeta potential on perchlorate adsorption

The effect of pH on perchlorate removal by AC and the resin was quite different as shown in Fig. 5a. Perchlorate removal by the resin remained unchanged in the pH range between 2.2 and 9.5. By contrast, perchlorate removal decreased from 80% to 38% when the pH increased from 2.2 to 9.3 when using AC. The effect of pH on perchlorate removal by virgin AC was investigated using rapid small-scale column tests (RSSCTs) [26]. Perchlorate breakthrough in the AC filter occurred at 1200 bed volumes at pH 8 whereas the breakthrough was observed at 2000 bed volumes

when the pH of solution was 6. At pH 4, the adsorption of perchlorate was significantly increased and the breakthrough occurred at approximately 3100 bed volumes. Xiong et al. [20] reported that perchlorate adsorption onto a SBA resin (IRA 900) was nearly independent of solution pH over the broad pH range of 2–12. However, the weak base anion (WBA) resin's tertiary amine groups became deprotonated with increasing pH, thereby losing anion exchange capacity.

When pH increased from 2.2 to 9.3, the zeta potential of AC decreased from approximately 9 to −75 mV without perchlorate (Fig. 5b). The point of zero charge pH (pH$_{PZC}$) was not shifted significantly in the presence of perchlorate (Fig. 5b). The adsorption of perchlorate did not change the zeta potential. The decreasing perchlorate removal by AC was coincident with its decreasing zeta potential in the pH range studied. The result suggested that perchlorate was associated with pH-dependent functional groups, such as hydroxylic, carboxylic, and phenolic groups, on the AC surface. Moore [27] reported that AC had a greater positive charge when the pH was reduced. It is understandable that there will be less electrostatic attraction between the surface and perchlorate anion when the surface potential decreases, which will decrease perchlorate adsorption. However, it should be noted that even when the surface was highly negatively charged, there was still more than 30% perchlorate removal. The results indicate that there might be specific chemical interactions between the perchlorate and the surface sites on AC.

The zeta potential of SR-7 resin was approximately 40 mV in the pH range of 4–9.5 (Fig. 5b). The results indicated that the positive charges of the quaternary amine functional groups on the resin were not affected by the pH change. Therefore, perchlorate adsorption by the resin remained constant over the pH range (Fig. 5a). The adsorption of perchlorate on the resin unexpectedly increased the zeta potential to about 60 mV. Further experimental results shown in Fig. 6 confirmed that the zeta potential increased when the perchlorate load on the resin increased to 80 mg/g. The removal of perchlorate involved exchange of perchlorate with chloride on the resin. The increased zeta potential could be attributed to displacement of more than one chloride anion by an adsorbed perchlorate anion due to steric effects. Since the anion volume of perchlorate (0.082 nm^3) is larger than that of chloride (0.047 nm^3) [28], it would occupy more space on the resin than chloride. Since the experiments were conducted in 0.2% NaCl solution, the resin sites could be saturated by chloride, which would also contribute to the increased zeta potential caused by perchlorate adsorption.
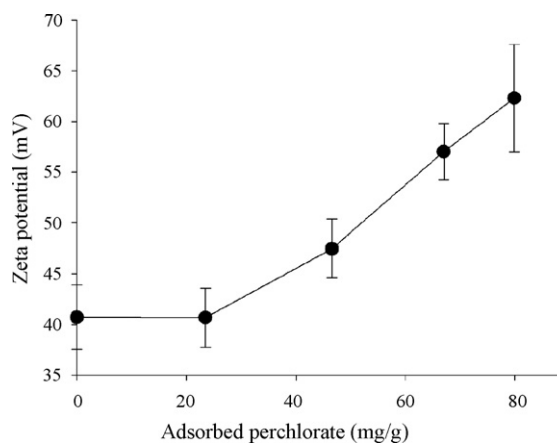

Fig. 6. Zeta potential of SR-7 resin as a function of perchlorate load, 0.2% NaCl solution, final pH 7.0 ± 0.5.
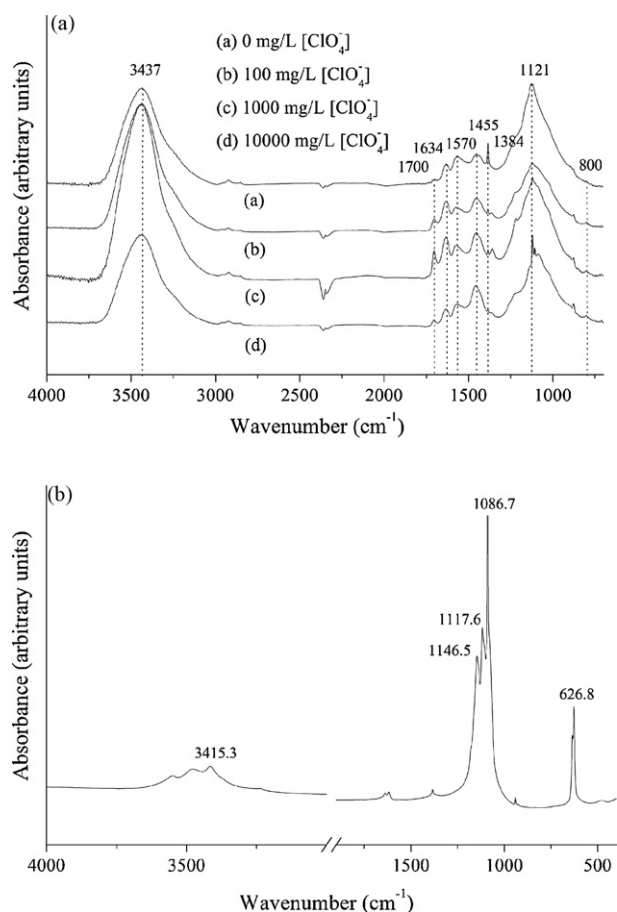
Fig. 7. (a) FTIR spectra of AC and perchlorate-loaded AC with baseline-correction, smoothed using the Savitzky–Golay method, and vertically stacked. Perchlorate-loaded AC samples were prepared by mixing the adsorbent with 10^2, 10^3 and 10^4 mg/L ClO$_4$ solution (b) FTIR spectrum of solid sodium perchlorate.

3.4. FTIR analysis of the AC surface

There are various surface functional groups on AC, such as carboxyl, phenolic hydroxyl, carbonyl, carboxylic acids, anhydrides, lactone, and cyclic peroxides [29–31]. The surface functional groups of AC and perchlorate-loaded AC were characterized using FTIR and the spectra are displayed in Fig. 7a. Infrared band assignments corresponding to chemical bonds on the AC samples are summarized in Table 1. Fig. 7b shows that solid NaClO$_4$ had a strong peak at 1086 cm^{-1}. A close examination of the AC spectra reveals that a small peak appeared near 1100 cm^{-1} when perchlorate was adsorbed on AC (Fig. 7a).

Table 1
FTIR spectrum band assignment of activated carbon

Wavenumber (cm^{-1})	Assignment	References
3437	O–H stretch of surface hydroxylic, carboxylic, and phenolic groups	[30,37]
1700	C=O stretch of carboxylic acid group	[30]
1634	C=O stretch of ketone	[37]
1570	C=C stretch of aromatic ring	[29,30,37]
1455	CH asymmetric deformation of alkane	[37]
1384	CH deformation of alkane	[31,37]
	–O– Asymmetric stretch of cyclic ether group	
1126	OH hydroxylic group	[29,30]
	C–OH stretch of phenolic structure	
801	C–H vibration	[31]

Since perchlorate could be adsorbed on negatively charged AC (Fig. 5), it must be associated with some functional groups on AC. Wang et al. [31] suggest that pertechnetate (TcO$_4^-$) can be associated with two binding sites, R–C–OH and R–C=O, where R represents aromatic rings. Pertechnetate (TcO$_4^-$) and perchlorate (ClO$_4^-$) anions are large and poorly hydrated with similar chemical properties. Pertechnetate is adsorbed on the R–C–OH site by displacing the hydroxyl group as described in reaction R–C–OH + TcO$_4^- \rightarrow$ R–C–OTcO$_3$ + OH$^-$. Our batch adsorption results indicated that when AC was mixed with 500 mg/L perchlorate, the solution pH increased from 6.6 to 8.4, indicating the release of OH$^-$ ions. When AC was mixed with a solution without perchlorate, the solution pH slightly increased from 6.0 to 6.5. Perchlorate might also be associated with the R–C=O site through R–C–OH in a R–C–OH + ClO$_4^- \rightarrow$ R–C–OClO$_3$ + OH$^-$ complex.

Wang et al. [31] proposed that pertechnetate could be associated with the R–C=O site through hydrogen bonding or electrostatic attraction, R–C=O$\cdots$H$^+$ + TcO$_4^- \rightarrow$ R–C=O$\cdots$H$\cdots$OTcO$_3$, with no net consumption or release of H$^+$. Selvasekarpandian et al. [32] reported that the 1730 cm^{-1} band which corresponds to the C=O stretching frequency of pure poly vinyl acetate (PVAc) was broadened and shifted to lower wave number (1706 cm^{-1}) when LiClO$_4$ was adsorbed on the solid. The change in the 1730 cm^{-1} band was attributed to the coordination of the lithium cations and perchlorate anions with the ester oxygen and C=O in the poly (vinyl acetate)–lithium perchlorate (PVAc–LiClO$_4$) complex. Perchlorate might also be associated with the R–C=O site through hydrogen bonding in a R–C=O$\cdots$H$\cdots$OClO$_3$ complex.

3.5. Raman spectroscopy characterization of perchlorate

Raman spectra of different forms of perchlorate are presented in Fig. 8 and the characteristic peaks are summarized in Table 2. Perchlorate in a 10% NaClO$_4$ solution had a characteristic perchlorate peak at 933 cm^{-1}. Mosier-Boss and Lieberman [33] reported a peak at 935 cm^{-1} for an aqueous perchlorate solution. The appearance of the strong band at 934 cm^{-1} was ascribed to the symmetric (ν_1) vibration of the perchlorate anion [34].
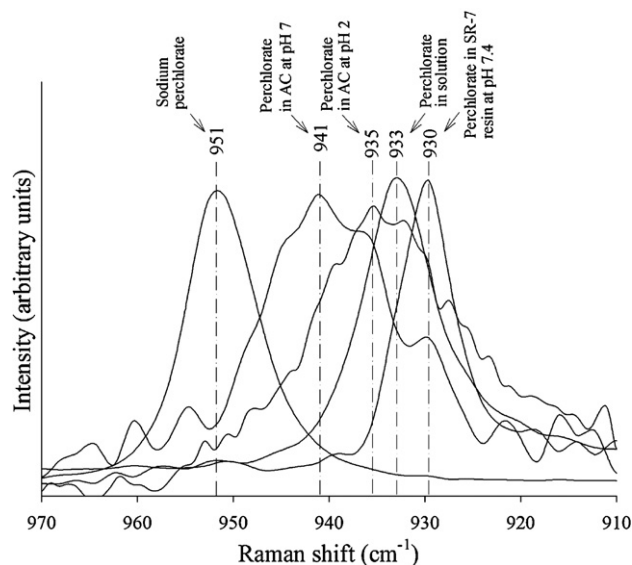

Fig. 8. Raman spectra of perchlorate in solid sodium perchlorate and aqueous perchlorate solution, and on AC at pH 7 and 2, and on SR-7 resin at pH 7.4.

Table 2
Raman band frequencies of the ν_1 (perchlorate) mode for sodium perchlorate, perchlorate solution, AC, and SR-7 resin used in this study

Samples	ν_1 (perchlorate) stretching (cm^{-1})	Peak assignment[a]
Perchlorate solution (pH 2–7)	933	Free anions
Perchlorate adsorbed SR-7 resin (pH 7.4)	930	Free anions
Perchlorate adsorbed AC (pH 7)	941	Contact ion pairs
Sodium perchlorate	951	Trimers or tetramers

[a] Compared with Selvasekarpandian's Raman band frequencies of the ν_1 (perchlorate) [32]. Free anions: 934 and 933 cm^{-1}; contact ion pairs (Li$^+\cdots$ClO$_4^-$): 939 cm^{-1}; trimers or tetramers (Li$^+\cdots$ClO$_4^-\cdots$Li$^+$): 945 cm^{-1}.

The ν_1 symmetric stretching mode of the anion is sensitive to ion association and ion–ion interactions [35]. Selvasekarpandian et al. [32] reported that Raman bands at 934 and 939 cm^{-1} correspond to free perchlorate anions and contact ion pairs (Li$^+\cdots$ClO$_4^-$) in poly (vinyl acetate)–lithium perchlorate, respectively. A Raman band of perchlorate at 945 cm^{-1} was attributed to trimers (Li$^+\cdots$ClO$_4^-\cdots$Li$^+$), tetramers or higher order ionic clusters of sub-micron scale [32].

The peak position of the adsorbed perchlorate on the resin was at 930 cm^{-1}, which was similar to that of aqueous perchlorate (Fig. 8). Gu et al. [36] also observed a perchlorate peak at 930 cm^{-1} for adsorbed perchlorate on a bifunctional anion-exchange resin (Purolite A-530E). The results indicated that there was no chemical interaction between the adsorbed perchlorate and the resin. It suggested that perchlorate was adsorbed on the resin surface through electrostatic attraction between the anion and the positively charged quaternary amine site.

Adsorption of perchlorate on AC at pH 7 resulted in a relatively large peak shift to 941 cm^{-1} (Fig. 8), suggesting that perchlorate was associated on the AC surface through interactions stronger than electrostatic forces. The Raman results were consistent with the observation (Fig. 5) that perchlorate was adsorbed on a negatively charged AC surface. The adsorbed perchlorate on AC at pH 2 showed a peak at 935 cm^{-1}, indicating that most of the perchlorate was adsorbed through electrostatic attraction. Raman spectra obtained for aqueous perchlorate indicated that the position of perchlorate peak remained at about 933 cm^{-1} at pH 7 and 2. Solid sodium perchlorate exhibited a peak at 951 cm^{-1}, which was a large shift from the peak position of aqueous perchlorate (Fig. 8). This indicated the bonding environment of perchlorate in the solid was quite different from that of free perchlorate ion in the solution. Perchlorate may exist in trimers (Na$^+\cdots$ClO$_4^-\cdots$Na$^+$) or higher order ionic clusters in the solid.

4. Conclusions

Batch and column adsorption and desorption results demonstrated that perchlorate adsorption by AC and SR-7 resin was reversible and adsorption/desorption reached equilibrium within 30 min. Solution pH significantly affected perchlorate adsorption and the zeta potential of AC, while it did not influence perchlorate removal or the zeta potential of the resin. Raman spectra and zeta potential measurements suggested that perchlorate was associated with functional groups on AC through interactions stronger than electrostatic interactions. The adsorption of perchlorate on the resin caused a very small shift of the perchlorate peak in the Raman spectra, which indicated that the adsorbed perchlorate existed in a form similar to free perchlorate in solution. The results suggested that perchlorate was adsorbed on the resin through electrostatic attraction between the anion and positively charged surface sites.

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