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Kinetic and isotherm studies on perchlorate sorption by ion-exchange resins in drinking water treatment

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ABSTRACT

The ion exchange capacity of five cationic resins (A532E, A520E, A400E, PWA-5, PSR-2) with regard to perchlorate ion was examined in batch kinetics and isotherms. The specificity of each resin was calculated from batch kinetic tests and results confirmed that the A532E and PSR-2 resins are more specific than the others for perchlorate removal. Furthermore, these results show PSR-2 and PWA-5 resins follow a pseudo-first order relation whereas exchanges are better described by pseudo-second order relations. The rate limiting step of ion exchange process was identified, for A400E, A520E and A532E as being the intraparticular diffusion, while PSR-2 and PWA-5 resins have an ion exchange rate limited by the external diffusion. Finally, the isotherm experiments show that the ion exchange equilibrium for perchlorate can be modelled by Langmuir relation for all resins and confirm that perchlorate ions are fixed forming a monolayer without interaction between molecules. The Langmuir model results indicate the maximal exchange capacities for perchlorates are of the same order of magnitude for all resins (from 183 mg g^{-1} for A400E to 115 mg g^{-1} for A532E). However for the removal of traces of perchlorates in drinking water, the experimental results confirm the benefit of perchlorate specific resins A532E and PSR-2.

1. Introduction

Perchlorate in groundwater, soil or surface water can be naturally occurring (notably from Chilean caliche ore deposits) but it is more often a contaminant from human activities [1]. Perchlorate ammonium is used as an oxidant in rocket motors, fire arms but also pyrotechnics, explosives, batteries and airbags [2].

The perchlorate anion (ClO_4^-) is undesirable in the environment and a threat to human health. In the event of pollution of water resources and drinking water, treatment may be needed to comply with qualities limits. In each country, these limits are different. In USA, USEPA [3] reports that each state has a limit concentration for the drinking water. In Massachusetts and Maryland, this limit is 1 μg L^{-1}, while in Arizona and Nevada it is 14 and 18 μg L^{-1} respectively. In France, on the basis of an opinion of the French agency ANSES [4], health authorities have set 15 μg L^{-1} as the limit value for perchlorate in drinking water with a stricter limit, set at 4 μg L^{-1}, for pregnant women and infants. The impact of perchlorate on health mechanisms is in the functioning of the thyroid gland. Perchlorate replaces iodine and thus inhibits the production of T3 and T4 [5–7].

Perchlorate salts (e.g. ammonium or potassium) are highly soluble in water. The perchlorate oxyanion is kinetically inert to reduction and weakly adsorbs onto organic and inorganic surfaces [8]. The persistence of perchlorate in groundwater is due to another property: a high mobility by diffusion and convection in the environment.

Various materials and technologies have been used to remove perchlorate from drinking water. Different authors [7–9] have written reviews on treatment methods for the perchlorate removal in water. These technologies are classified in 5 groups: (1) physical removal by the sorption on materials (powder or granular activated carbon alone or modified, granular ferric hydroxide or quaternary amine modified, synthetic organosilicas or ion-exchange resin). Many adsorbents can be used, but this requires further research on production parameters. (2) Chemical reduction by metal, metal ion, or hydrogen gas. These technologies are however very complex to be used in the drinking water treatment. (3) Biodegradation with some bacteria (using perchlorate like an electron acceptor for their metabolism). Perchlorate ions are reduced to chlorate (ClO_3^-), then to chlorite (ClO_2^-) and the final step is the chloride ion and oxygen production. This process is only possible under certain conditions (absence of nitrate, anaerobic conditions and high concentration).

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Table 1
Characteristics of each resin [10–14].

Resins	Capacity (eq L^{-1})	Polymer structure/functional group	Specificity	Density
PSR-2	0.65	Gel/quaternary amines	Perchlorate	1.10
PWA-5	>1.0	Macroporous strong base anion resin/quaternary amines	Nitrate	NC[a]
A400E	1.30	Gel strong base anion resin/quaternary Ammonium	Non-specific	1.08
A520E	0.90	Macroporous strong base anion resin/quaternary ammonium	Nitrate	1.07
A532E	0.80	Gel/bifunctional quaternary amines	Perchlorate	1.04

[a] NC, non-communicated.

(4) Electrochemical reduction on metal electrodes (tin, platinum, rhodium, nickel or titanium). The perchlorate reduction is possible in an acidic solution but this technology is expensive, and (5) integrated technologies coupling two methods to eliminate the pollutant.

The best method to remove perchlorate at low concentration in drinking water is the ion exchange. This treatment has some advantages, for example the possibility to eliminate a low perchlorate concentration (typically < 50 μg L^{-1}) with a good yield in the process that can be operated at a high or low flow. However, the anion exchange resin used should be selected according to their exchange capacity, stability, selectivity and regeneration capacity [7–9]. This last parameter is a problem for drinking water companies. Regeneration with sodium chloride (NaCl) is not efficient in that case. The use of $FeCl_3$-HCl at high temperature would be the only possibility for resin regeneration. This regeneration process is not acceptable for drinking water treatment and it is usually considered that the specific perchlorate resins cannot be regenerated. The exhausted resin is a waste product that must be discarded and replaced.

For drinking water treatment, where perchlorate concentrations are generally very low compared to other anions (typically 1–1000), the specificity and exchange rate are key factors for effective removal. However, the selection of the most appropriate resin depends on each specific situation (water composition, temperature, treatment needs, etc.) and requires case-by-case evaluation. The service life of the resins is also an important factor as they are not regenerable when used for perchlorate removal.

The objective of this paper is to compare 5 commercially available ion exchange resins for the removal of trace perchlorate concentrations in water. In the first instance, the ion-exchange kinetics are investigated to decipher the ion exchange mechanisms by fitting the experimental data to kinetic models. In the second instance, the isotherm experiments were carried out to determine the best model (Langmuir, Freundlich) to describe the perchlorate equilibrium between the liquid phase and the resin.

2. Materials and methods

2.1. Ion exchange resins and chemicals

Isotherms and exchange kinetics experiments were conducted with 5 ion-exchange resins (Table 1) which were selected for their capacity of perchlorate removal. The first is a non-selective resin, A400E (Purolite®). The 2 next resins have a higher affinity for nitrate (A520E by Purolite® and Amberlite PWA-5 by Rohm & Haas®). Finally, the last two resins have a strong selectivity for perchlorate (A532E by Purolite® and PSR-2 by Dow®). PWA-5, A520E and A400E are approved for use for drinking water treatment in France for nitrate, while PSR-2 and A532E have not been approved yet. In Table 1, the characteristics for each resin are presented.

The initial solution of perchlorate is 1000 mg L^{-1} in ultrapure water (mono-element standard solution, CaPurAn Chem). For the batch kinetic studies, tap water has been used to obtain nitrate and sulphate ions. The tap water is a medium mineralized water (conductivity ~600 μS cm^{-1}, alkalinity ~200 ppm $CaCO_3$ and hardness ~250 ppm $CaCO_3$). Concentrations of other anions are given in Table 2.

2.2. Chemical analyses

The concentrations of perchlorate, nitrate, sulphate and chloride were monitored by ion chromatography (ICS 2000, Dionex). The parameters of analyses are listed in Table 3. The analyzer is equipped with an eluent generator (KOH) and a suppressor for reducing the conductivity of the eluent, thus improving the sensitivity of the assay.

2.3. Ion-exchange kinetics in batch

In batch kinetic experiments a set amount of resin was introduced into a flask containing exactly 2 L of deionised water spiked with perchlorate ions ($C_0 \approx 10$ mg L^{-1}). Previously, the resin (dried mass around 1.0 g) was conditioned for 24 h in ultrapure water under shaking (150 rpm) at 25 °C. In Table 2, the experimental parameters are presented for kinetics with and without competitive ions (sulphate and nitrate).

Anions concentrations have been measured by ion chromatography on 13 successive samples (20 mL) taken at various times (0, 1, 3, 5, 7, 10, 12, 15, 20, 30, 40, 50, 60, 90, 120, 150, 210, 330, 420, 1450, 1710 min).

The amount of fixed perchlorate or other ions has been calculated by mass balance (Eq. (1)). The chloride concentration was measured to confirm the exchange between perchlorate and chloride ions on the resin. The stoichiometry of the chemical reaction is one for one: a milliequivalent chloride is released for one milliequivalent perchlorate exchanged.

$$n_{Initial\ A^-} = n_{re\sin\ A^-} + n_{solution\ A^-} \qquad (1)$$

with $n_{Initial\ A^-}$, the initial amount of anion (meq); $n_{solution\ A^-}$, the amount of anion at any time in water (meq) and $n_{resin\ A^-}$, the anion amount fixed on the resin (meq).

Table 2
Experimental parameters for batch kinetics.

Kinetics	T	Stirring (rpm)	$[ClO_4^-]_0$ (mg L^{-1})	$[NO_3^-]_0$ (mg L^{-1})	$[SO_4^{2-}]_0$ (mg L^{-1})
ClO_4^- in deionised water	25	150	≈10	0	0
ClO_4^- in tap water	25	150	≈10	25	25

Index 0, initial concentration.