Chemical Engineering Journal 223 (2013) 309–317

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Effect of preparation protocol on anchoring quaternary ammonium/epoxide-forming compound into granular activated carbon for perchlorate adsorption: Enhancement by Response Surface Methodology

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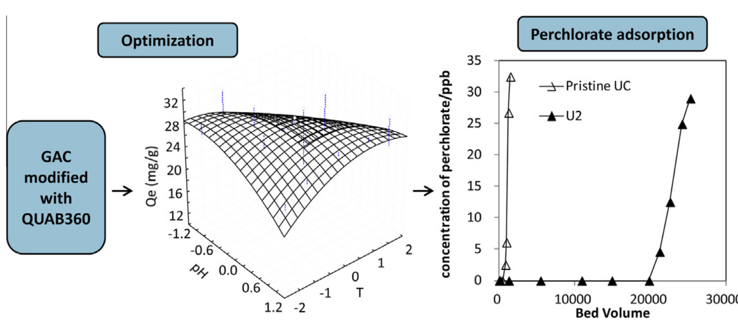
HIGHLIGHTS

- A novel tailored GAC has been developed for removing perchlorate from groundwater.
- A statistical method was used to appraise the effect of the preparation protocol.
- A Response Surface Methodology was used to find the more favorable tailored GAC.
- We tested perchlorate removal capacity of the more favorable tailored GAC by RSSCT.
- We investigated the effect of preparation conditions on tailored GAC's properties.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 December 2012
Received in revised form 28 February 2013
Accepted 2 March 2013
Available online 14 March 2013

Keywords:
Granular activated carbon (GAC)
Quaternary ammonium/epoxide-forming compound (QAE)
Perchlorate adsorption
Response surface methodology (RSM)
Rapid small scale column tests (RSSCTs)

ABSTRACT

A novel method has been developed for anchoring quaternary ammonium/epoxide-forming compounds (QAEs) within bituminous based granular activated carbons (GACs). This modified GAC was then used to remove perchlorate from groundwater. The effect of the preparation temperature (*T*), solution pH (pH) and the dry mass ratio of QAE-to-GAC (*R*) over the perchlorate adsorption capacity (Q_e) were studied by the Response Surface Methodology. The combined effects of these variables were fitted to a quadratic model to determine the more favorable preparation protocol for perchlorate removal. Statistical analysis revealed that: (1) the interaction of *T* and pH incurred the most effect on Q_e; and (2) two of the more favorable preparation protocols became apparent: one was at 75 °C, pH 11 and *R* of 1.73 g QAE/g GAC (U17), the other was at 35 °C, pH 14 and *R* of 4.00 g QAE/g GAC (U2). Rapid small scale column tests were further employed to evaluate the performance of the QAE-anchored GACs for perchlorate removal. U17 and U2 exhibited 18–20 times longer bed life (BV) to 6 ppb breakthrough than did the Pristine GAC (900 BV), when processing groundwater that had been spiked with 30–35 ppb perchlorate. This indicated the statistical method enhanced GAC's perchlorate removal efficiency.

1. Introduction

Granular activated carbon (GAC) has been widely applied as an adsorbent for organic contaminants, but less frequently for adsorbing negatively-charged oxyanions from water and wastewater [1]. Perchlorate is a pollutant that has been detected in drinking water in 26 US states and Puerto Rico [2]. In the human body, perchlorate can inhibit thyroid hormone production, which is

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http://dx.doi.org/10.1016/j.cej.2013.03.006

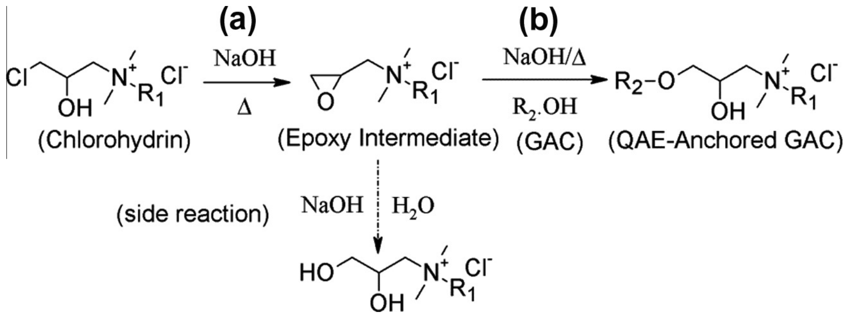


Fig. 1. Proposed schematic of QAE-anchoring process (R_1 = alkyl tail in QAE compound, R_2 = polyaromatic graphene layers in granular activated carbon).

essential to normal organ development in infants, especially brain development [3]. In 2008, the USEPA set an Interim Drinking Water Health Advisory level of 15 μg/L [4]. Some states have lower action levels such as 6 ppb in California and 2 ppb in Massachusetts [5].

In this study, the authors developed a novel method to remove perchlorate from groundwater by anchoring a quaternary ammonium/epoxide-reacting compound (QAE) into activated carbons by means of an epoxide-forming reaction. The QAE molecules consist of an epoxide-forming functionality, a quaternary ammonium functional group, and a surfactant tail [1]. The epoxide-forming end of such a molecule could anchor to the GAC, while the quaternary ammonium group could preferentially exchange a carrier anion for perchlorate. The surfactant tail enhanced adsorption of these molecules into the GAC pores [1]. This work builds on previous Penn State research, wherein quaternary ammonium-surfactant compounds were loaded onto GAC, so as to subsequently adsorb perchlorate [6–9]. However, some of that loaded surfactant could desorb during water treatment and cause subsequent environmental pollution. In contrast, the advantage of the method herein is that it would preclude quaternary ammonium from subsequently leaching out of GACs, while also maintaining a high adsorption capacity for perchlorate [1].

The QAE-anchoring process involved three steps: (1) adsorbing QAE to the GAC's graphene layers; (2) reacting the epoxide-forming end of the QAE with the –OH groups on GACs or on another QAE molecule in presence of NaOH (Fig. 1a and b); and (3) rinsing the residual QAE with reagent alcohol.

The authors note that some of the variables that influence perchlorate removal have been addressed separately by Hou et al. [1], including the carbon source, QAE molecular weight and preparation time. Preliminary results also showed that the QAE anchoring process was highly influenced by the process temperature (T), pH and ratio of mass QAE (dry) to GAC (R). Therefore, it was perceived as desirable to discern the significance of each variable and the interaction between those three variables during the preparation process, and to appraise their influence on perchlorate adsorption capacity. This could help maximize the perchlorate removal efficiency of the QAE-anchored GACs. The conventional approach for optimization of process variables requires a very large number of experiments to be performed, which would be very time consuming. More importantly, it ignores the combined interactions between the process variables [10]. In contrast, statistical experimental design using Response Surface Methodology (RSM) can not only determine the relationship between various process parameters and the responses, but also further discern the significance of these process variables on the coupled responses, while carrying out only a limited number of experiments [11,12].

The RSM has been widely used in various fields such as in production of activated carbon from Luscar char, coconut shell and agave salmiana bagasse [13–15], and for improving performance of cationic starches [16–18]. Also, RSM has also been used for studying the optimization of the coagulation–flocculation process in water treatment [19]. However, no other known published studies have employed RSM specifically for appraising the more favorable preparation protocols for QAE-anchored GAC that is tailored to remove perchlorate from groundwater.

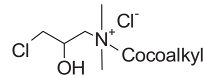
In view of the above perspective, the objectives of this study have been to: (1) anchor QAE by chemical bonding to the –OH groups on graphene layers' edge sites within GACs (or bonding to the –OH groups of other sorbed reagent molecules); (2) apply a three-factor central composite experimental design combined with RSM for examining the perchlorate-removal effects of three independent variables (T, pH and R that was used during the preparation protocol), while thus maximizing the adsorption capacity of the QAE-anchored GACs; (3) evaluate the performance of the selected QAE-anchored GACs in perchlorate removal via rapid small scale column tests (RSSCT), so as to find the more favorable QAE-carbon preparation protocol for perchlorate removal; and (4) study the relationship between the physical–chemical properties showed in characterization and the perchlorate adsorption capacity achieved during RSSCTs.

2. Experimental

2.1. Materials

Bituminous coal-based granular activated carbon, Ultracarb 1240, manufactured by Siemens Industry Inc. was used in this study, and designated as UC carbon hereafter. UC was presented as the more favorable carbon source for anchoring QAE per previous study [1]. Prior to use in the tailoring process, UC was ground and sieved to a US mesh size of 200 × 400 (38 × 75 μm) in order to be the appropriate size for proportional diffusivity similitude in RSSCTs. It was then washed with distilled–deionized water to remove fines, and dried at 95 °C overnight to remove moisture. The carbon sample was then stored in a vacuumed desiccator until use.

The QAE employed to produce the QAE-anchored GAC was QUAB360 (3-chloro-2-hydroxylpropylcocoalkyl-dimethyl-ammonium chloride) (40 wt% in water, with a density of 1 g/mL). The structure of QUAB360 was as shown below:



Deionized (DI) water was used for preparing analytical standards of perchlorate solutions and for adsorption isotherm experiments. DI water was treated by a Millipore Milli-Q Academic system, and it hosted an electrical resistivity of ⩾18.1 MΩ/cm^2. The water used in RSSCT experiments was raw groundwater taken from Well 17 at The Pennsylvania State University (PSU), and this groundwater had not received chlorination or any other chemical