



Adsorption of 4-chlorophenol and aniline by nanosized activated carbons



Chengyu Chen^a, Xinhua Geng^b, Weilin Huang^{a,*}

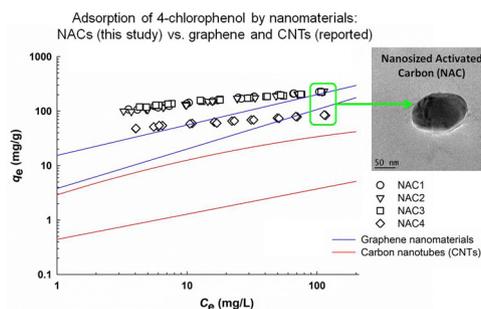
^a Department of Environmental Sciences, Rutgers, The State University of New Jersey, 14 College Farm Road, New Brunswick, NJ 08901, United States

^b School of Chemistry and Chemical Engineering, Guangzhou University, 230 Guangzhou University City Outer Ring Road, Guangzhou, Guangdong 510006, PR China

HIGHLIGHTS

- NACs have sorption capacity 10–100 times > other nano sorbents for 4-CP and aniline.
- NACs have large SSAs (900 m²/g) and microporosities (65% v/v).
- Adsorption follows pseudo-second-order rate model and Freundlich isotherm.
- Adsorption mechanism and effects of pH, *T*, and ionic strength were investigated.
- Highly stable and adsorptive NACs are potentially suited for groundwater remediation.

GRAPHICAL ABSTRACT



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ABSTRACT

Reactive solids injected into aquifers for *in situ* groundwater remediation should possess both high mobility and great reactivity or adsorption for targeted contaminants. We have shown in a prior study that nanosized activated carbons (NACs) had strong colloidal stability in aquatic environments. The present study investigated the adsorption behavior for the four NACs and two typical aromatic contaminants, 4-chlorophenol (4-CP) and aniline. The adsorption capacities measured for the NACs were compared with those reported for other nanosized adsorbents which were considered as potential candidates for groundwater remediation. Our results indicated that NACs had large specific surface areas (SSAs) and microporosities, and exhibited rapid rates of adsorption that could be quantified with both the pseudo-second-order rate equation and the intra-particle diffusion model. The adsorption equilibria were adequately described with the Freundlich isotherm equation, and hydrophobic interactions were likely the dominating mechanism for the adsorption. The adsorption processes were influenced by solution pH and temperature, whereas background electrolytes showed negligible effect. The tested NACs exhibited adsorption capacities 10–100 times greater for the respective adsorbates when compared to other carbonaceous nano-adsorbents such as carbon nanotubes (CNTs) and graphene derivatives. Such strong adsorbability, along with their high colloidal stability, makes NACs potentially suitable for remedy of aquifers contaminated with organic pollutants.

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1. Introduction

Injecting strongly sorptive and/or reactive solids into aquifers is a widely used engineering scheme for *in situ* remedy

* Corresponding author.

E-mail address: whuang@envsci.rutgers.edu (W. Huang).

of groundwater systems contaminated with toxic organic and inorganic chemicals [1]. The injected solids presumably not only are highly reactive, but also can remain suspended and can travel along with groundwater in polluted aquifers over long periods of operating time [2]. Searching for innovative nanomaterials that meet the two criteria has long remained a top priority in the field of groundwater remediation.

Manufactured carbonaceous nanomaterials have recently been considered as potential adsorbents for serving such remedial purposes because they have nano-structures, large specific surface areas (SSAs), controlled pore size distribution, and tunable surface chemistry, which overcome various intrinsic limitations of conventional carbonaceous adsorbents [3,4]. Indeed, their high sorption capacities and more stable colloidal properties may be better suited for decontamination of groundwater systems. Prior studies have quantified and compared the aqueous adsorption of pollutant onto various carbonaceous nanomaterials, such as carbon nanotubes (CNTs) (single-walled, SWCNTs or multi-walled, MWCNTs), graphene and derivatives (graphene oxides, GO or reduced graphene oxides, RGO), fullerenes (C_{60}), and carbon nanospheres (CNS) [4,5]. CNTs were shown to have more efficient adsorption of large size molecules due to their larger pore sizes compared to conventional activated carbons (ACs). However, due to their strong inter-particle interactions, pristine CNTs are prone to aggregation, forming settleable aggregates in aqueous solutions, which significantly reduces both the SSA available for pollutant adsorption and their mobility in porous media [6]. Surface functionalization of CNTs may alleviate their aggregation in water, but can lower their adsorption capacity for organic pollutants. For instance, the adsorption capacities of MWCNTs for synthetic organic compounds were reduced by 25–30% after surface functionalization [7]. With different structures and functional groups, two-dimensional graphene and its derivatives such as GO have adsorption capacities comparable to CNTs for both organic compounds and heavy metals, and are also more stable against aggregation compared to CNTs [1]. However, the reported toxicity and high costs of CNTs and GO nanomaterials are the major roadblocks preventing their potential application as adsorbents in water treatment [1,3]. Other manufactured carbonaceous nano-adsorbents, such as fullerene and CNS, have low SSAs of 0.07–10 [5] and 1.2–100 m^2/g [8], respectively, and thus exhibit much lower adsorption capacities compared to AC materials with large SSAs. For example, the adsorption capacity for naphthalene by fullerene was about 1000-fold lower than ACs [9].

Conventional AC materials are among the best adsorbents for water treatment due to their high adsorption capacities for a broad spectrum of pollutants, well understood adsorption mechanisms, and high cost-effectiveness [10]. Powdered activated carbon (PAC) materials with particle sizes ranging from a few to 40 μm are known as strong sorbents for various contaminants, but they could be readily immobilized in aquifer due to filtration mechanisms. They are apparently not ideal reactive solids for *in situ* groundwater remediation. Two prior studies proposed to utilize AC suspensions having particle sizes of 800 nm as a stable mobile adsorbent that could be injected into contaminated aquifers [11,12]. Nanosized activated carbons (NACs) with properties and adsorbability likely similar to conventional ACs may be better candidates. Meanwhile, NACs may have no obvious toxicity or adverse effect as revealed by clinical and biological studies using NACs as drug carriers and as disease tracers during surgery treatments [13–16]. However, few studies have examined their adsorption properties for organic (e.g., methyl orange dye [17] and organophosphorus malathion pesticide [18]) and inorganic pollutants (e.g., arsenic [19] and copper [20]) in aqueous solutions.

The goal of this study was to quantify the adsorption properties for four NACs in an effort to assess their applicability

in groundwater remediation. In a prior study [21], we found that NACs have high colloidal stability against aggregation under typical freshwater chemistry conditions. Herein, the four types of NACs investigated in that prior study were chosen to investigate their adsorption behavior for two aromatic pollutants, 4-chlorophenol (4-CP) and aniline, in aqueous solutions. These two target pollutants were chosen because chlorophenols and anilines are toxic, carcinogenic, and environmentally related contaminants commonly found in groundwater [22–26]. The results showed that their adsorption capacities were one or two orders of magnitude greater when compared with other nanosized adsorbents that were considered in prior studies as potential active reagents. The strong adsorption, along with high colloidal stability, makes NACs better candidates for remedy of contaminated groundwater systems.

2. Materials and methods

2.1. Adsorbents

The four NACs purchased from US Research Nanomaterials, Inc. (Houston, TX) were assigned as NAC1, NAC2, NAC3, and NAC4, which were the same nanomaterials investigated in our prior study [21]. According to the supplier, the four NACs were produced from a selection of different plant materials (Table 1) through carbonization, activation, grinding, and classification. For better comparison with the four NACs, a commercial Hydrodarco®C PAC produced via steam activation of lignite coal was also obtained from Norit Americas Inc. (Marshall, TX) and used as the fifth adsorbent. These five AC adsorbents were stored in a desiccator prior to use.

2.2. Characterization of adsorbents

The porous structures of the adsorbents were characterized using the methods of N_2 gas adsorption-desorption isotherms obtained at 77 K on a Micromeritics TriStar II 3020 instrument (Micromeritics Instrument Corp., Norcross, GA), yielding results of the SSA and the pore distribution using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The size and morphology of the adsorbents were examined on a scanning electron microscope (SEM) (MERLIN, Zeiss, Oberkochen, Germany) and on a transmission electron microscope (TEM) (Topcon 002B, Topcon Corp., Tokyo, Japan) operating at 200 kV. The hydrodynamic sizes of NACs were measured in water by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS instrument (Malvern Instruments, Worcestershire, UK).

2.3. Chemicals and solutions

Aniline (ACS grade, +99%) and 4-CP (+99%) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO) and Alfa Aesar (Ward Hill, MA), respectively, as the target pollutants. The selected physicochemical properties of the adsorbate chemicals are presented in Table 2. Calcium chloride, sodium azide, acetic acid, hydrochloric acid, and sodium hydroxide of ACS grade were obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO). Methanol and acetonitrile of HPLC grade were purchased from Honeywell International, Inc. (Morris Plains, NJ) and EMD Millipore (Billerica, MA), respectively.

Stock solutions of the adsorbates at 1000 mg/L were prepared by dissolving their pure liquids in background solution containing 10 mM $CaCl_2$ in Milli-Q water (resistivity of 18.2 $M\Omega cm$) with 200 mg/L sodium azide (NaN_3) as a biocide. All working solutions of desired solute concentrations were prepared by successive dilution of respective stock solutions with the background solution.

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