

Availability of Safe Drinking Water

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INTRODUCTION

Mass production and development of commercially available nanomaterials (NM) has the potential to adversely impact the removal of organic contaminants using activated carbon. The American Society for Testing Materials defined NM as a material with one dimension less than 100 nm. Nanoparticle (NP) is a subgroup of NM with at least two dimensions less than 100nm. In recent years, the manufacturing of synthetic NM has grown spectacularly. This includes many different compounds such as metal oxides; semiconductor materials, including quantum dots; zero-valent metals such as iron and silver. The high production and use of the NM is manifested by high release of NP into the environment and consequently to natural water. Zero valent iron is one of the most common NP that could find their way into the water system because of their use in water and soil treatment. Other NP of concern could also be nano TiO₂ or even nano silica. More studies are needed to understand the fate and transport of NP in water and their impact on the conventional water treatment methods.

Trichloroethylene (TCE) is a volatile organic carbon (VOC) that is commonly used as a cleaner in industry. This solvent is also used in metal finishing, electrical component, paint and ink formulation, and rubber processing wastewaters. Due to its negative impact on the ecosystem and human's health, which can be as severe as increased risk for cancer, TCE is regulated by the USEPA to a low level of (MCL= 5µg/l). Due to TCE's extensive commercial use and inappropriate waste disposal, TCE has become a main environmental pollutant.

Activated carbon (AC) has been regarded by USEPA as the best available technology for removing VOCs. However, the presence of background materials in natural water can highly impact this process. Natural organic matter (NOM) is the product of the breakdown of dead plants and animals. NOM is present in the environment in high concentrations and molecular weights. NOM can affect the AC adsorption through one of the following two avenues. The low molecular weights NOM can reduce VOCs adsorption by competing with the VOCs for adsorption sites. On the other hand, the larger molecular weight NOM usually decreases VOC adsorption through AC pore blockage that can lead to AC fouling. NPs may have an effect similar to that of NOM on TCE adsorption. It is known that NPs aggregate in water and form larger particles. According to their electrical charge and the water pH and ionic strength, these larger particles can get attached to the carbon and damage or block the adsorption pores and subsequently reduce the surface area and the amount of TCE adsorbed. Another scenario could be the behavior of these NPs as adsorption sites; this could be the most likely situation for the Zero -valent iron.

The fate of NPs in the environment is yet to be fully understood. Like VOCs, the production of NMs is estimated to be in millions of tons per year. The effects of these substances when released into aquatic systems are not clear. Moreover, little is known regarding the interaction of NMs and VOCs, and the impact of this interaction on the removal of VOCs from water. This study will increase the understanding of NM behavior in regards to VOCs removal by AC. This knowledge is vital due to the severe health risks imposed by VOCs. On the other hand, NPs take a very long time to settle, thus they are likely to be carried by water, along with other hazardous adsorbates, to the consumer.

In the state-of-the art Environmental Chemistry Laboratory, participating teachers will conduct batch TiO₂ with or without background NOM adsorption studies by employing vials with Teflon caps. The main objective of this study is to evaluate the impact of nano TiO₂ on the effectiveness of AC adsorption of the TCE.

MATERIALS AND METHODS

Adsorbates:

TCE obtained from Sigma-Aldrich at 99.9±% purity. Humic acid (a representative of NOM) is obtained from Aldrich chemicals in powder form with purity over 99%. TiO₂ industrial APS powder at a particle size range of 20 to 40 nm obtained from Alfa Aesar.

Adsorbents:

Calgon Inc filterasorb 400 (F-400) will be used for all the isotherm studies. The F-400 will be crushed into powder activated carbon (PAC) before being used for the isotherm studies.

Organic-free water:

Solutions of the adsorbates will be prepared in autoclaved deionized (DI) water buffered with 0.01M KH₂PO₄, and the pH adjusted to 7.0 with a 10 M solution of NaOH. The total organic carbon concentration of the DI water used in this study is expected to be less than 0.2mg L⁻¹.

Adsorption Isotherm Procedure:

The bottle point method will be used for conducting the adsorption isotherms at room temperature. Adsorption isotherms will be conducted at initial concentrations of TCE (1800 µg/L). Two different TiO₂ NP concentrations will be considered, namely, 0.5 and 0.1 mg/L in the presence and absence of 5 mg/L humic acid. The two TiO₂ concentration levels are used to study the impact of NP concentration on adsorption. Accurately weighed (± 0.1 mg) masses of PAC are placed in 250-mL glass amber bottles. Four liters of the adsorbate solutions will be prepared in autoclaved de-ionized water buffered as stated above and mixed for one hour. The 250-mL glass-amber bottles containing the different masses of carbon are then completely filled with the adsorbate solution, sealed tightly with Teflon lined caps and covered by parafilm. The bottles are then allowed to equilibrate in a rotary tumbler for a period of 10 days. For each set of isotherms 8 bottles need to be prepared. Table 1 lists the different experimental set up for the different adsorbates.

Table 1. Experimental set up for the adsorption isotherm study

Compound	Background Matrix	Adsorbents
TCE	Deionized water	PAC
TCE	Deionized water + 0.5 and 1.0 mg/l TiO ₂	PAC
TCE	Deionized water + 0.5 and 1.0 mg/l TiO ₂ + 10 mg/L humic acid	PAC

Analytical procedure:

After equilibrium, samples from each bottle were filtered through a 0.45 µm filter, diluted, and analyzed using an Archon 5100 Purge & Trap Autosampler connected to a Tekmar 3000 Purge & Trap Concentrator. The purge and trap unit is interfaced to a Hewlett Packard 6890 gas chromatograph (GC) equipped with a flame ionization detector (FID).

Prior to analyzing the experimental isotherm samples, the GC has to be calibrated for TCE. Tetrachloroethane (PCE) was used as an internal standard at a concentration of 25µg/L. A calibration curve is generated by using six different concentration levels of TCE (15, 30, 50, 100, 200, and 300). These concentrations are obtained by diluting a 20mg/l stock solution. The calibration curve is determined by using linear regression analysis of the peak area of the compound determined in the GC and the theoretical concentration of the compound of interest (TCE). The regression analysis should be done by using Excel spreadsheet program. The regression coefficient (R^2) should be greater than 0.95. In order to evaluate the goodness of the regression analysis, the following procedure is used. In Excel worksheet enter the peak area and the theoretical concentration corresponding to each peak area. A third column is generated for providing the response factor at each concentration level. The response factor (RF) is defined as follows:

$$RS = \frac{\text{Theoretical Concentration}}{\text{Peak Area}}$$

The average response factor is then determined. A fourth column is then generated for providing the coefficient of variation. The coefficient of variation (CV) is defined as follows:

$$CV = \frac{|\text{Average Response} - \text{Response Factor}|}{\text{Average Response}} \times 100$$

The CV for each concentration level should be less than 10%. If it is more than 10 %, the analysis for this calibration point is repeated again.

Once a good calibration curve has been determined ($R^2 > 0.95$ and $CV < 10\%$), the experimental samples obtained from the isotherm bottles can then be analyzed. The concentrations determined by using the calibration curve is then used to determine the amount adsorbed. The amount adsorbed is determined by the following equation:

$$q_e = \frac{(C_o - C_e) \cdot V}{m}$$

Where q_e = the amount adsorbed µg/g of adsorbent

C_o = initial concentration of the adsorbate (TCE), µg/L

C_e = equilibrium concentration of adsorbate TCE), µg/L

V = volume of solution in the sotherm bottle, 250 mL

m = mass of PAC in the isotherm bottle, g

The data collected is then analyzed against two well known isotherm equations, Langmuir and Fruendlich. The analyses against these equations are run by using regression analysis in Sigmaplot Software. This software has a powerful plotting technique and generates also a report for the regression analysis. The Langmuir equation is given by:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$

where Q_0 and b are regresi3n parameters.

The Freundlich isotherm equation is given by:

$$q_e = kC_e^{1/n}$$

where k and 1/n are regression parameters. The regression is best done by using a logarithmic form of the above equation.

The results obtained are then discussed to see the impact of TiO₂ NPs on the on the adsorption behavior of TCE in the presence and absence of humic acid.

In a similar fashion, the analysis for humic acid is conducted for the isotherms run with a background of humic acid. . Samples from the isotherm bottles will be taken and filtered through 0.1 µm membrane filters and then analyzed by using high performance liquid chromatography (HPLC). A calibration curve will be first determined by using a solution containing 10 mg/L of humic acid and analyzed in the HPLC by injecting different volumes so that a calibration curve can be generated based on the mass of humic acid injected.

Final Report:

The final report should be presented in the form of any published article in a journal. It should include the following sections in the order stated: Abstract, Introduction, Experimental Methods and Procedure, Experimental Results and Discussion, Conclusion, and References.

Time line of the project: The time line of the project is given in table 2

Table 2: Project timeline

Date	Expected Outcome
First & Second week	Prepare isotherm bottles for TCE with and without humic acid on PAC; and also prepare calibration curve for TCE and humic acid
Third Week	Prepare isotherm bottles for TCE with 0.5 and 1.0 mg/L TiO ₂ Without humic acid on PAC.
Fourth Week	Analyze samples prepared in three weeks. Prepare regression analyses for all experimental samples collected.
Fifth Week	Prepare isotherm bottles for TCE with 0.5 and 1.0 mg/L TiO ₂ and 0.5 mg/L humic acid on PAC.
Sixth Week	Analyze samples prepared in the fifth week. Prepare regression analyses for all experimental samples collected.

Laboratories Facilities

Environmental Chemistry Laboratories

These laboratories have about 1,000 sq. ft of contiguous research space which houses one laboratory for wet chemistry experiments and four laboratories that are well equipped with state-of-the-art equipment for analytical studies. The laboratories have two gas chromatography (GC) instruments, with dual detectors

(FID and ECD) for analyzing a wide variety of organic species, one high pressure liquid chromatograph (HPLC) with diode array detectors are available for analyzing nonvolatile compounds, one gas chromatograph/mass spectrometers (GC/MS) for specific compound determination in complex environmental samples, a Paragon 1000 FTIR Spectrometer for measuring interactions with surfaces and absorbates, an Analyst 300 Furnace and Flame Atomic Absorption Spectrometer for measuring aqueous metal concentrations down to parts per billion with the graphite furnace accessory, a Shimadzu UV Mini1240 Spectrophotometer for measuring the UV-VIS absorption spectra of a wide variety of compounds, and one Shimadzu Total Organic Analyzers for measuring total organic and inorganic carbon by combustion followed by infrared detection. Several pH and conductivity meters, as well as, analytical balances are available. The laboratories are also equipped with a dual level rotary tumbler for providing the necessary mixing for adsorption equilibrium studies.



Batch Studies Experimental Setup



A Gas Chromatograph with FID and ECD

References:

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