Activated carbons from flax shive and cotton gin waste as environmental adsorbents for the chlorinated hydrocarbon trichloroethylene


Abstract

Agricultural by-products represent a considerable quantity of harvested commodity crops. The use of by-products as precursors for the production of widely used adsorbents, such as activated carbons, may impart a value-added component of the overall biomass harvested. Our objective in this paper is to show that flax shive and cotton gin waste can serve as a precursor for activated carbon that can be used for adsorption of trichloroethylene (TCE) from both the liquid and gas phases. Testing was conducted on carbon activated with phosphoric acid or steam. The results show that activated carbon made from flax shive performed better than select commercial activated carbons, especially at higher TCE concentrations. The activation method employed had little effect on TCE adsorption in gas or vapor phase studies but liquid phase studies suggested that steam activation is slightly better than phosphoric acid activation. As expected, the capacity for the activated carbons depended on the fluid phase equilibrium concentration. At a fluid concentration of 2 mg of TCE/L of fluid, the capacity of the steam activated carbon made from flax shive was similar at 64 and 80 mg TCE/g of carbon for the vapor and liquid phases, respectively. Preliminary cost estimates suggest that the production costs of such carbons are $1.50 to $8.90 per kg, depending on activation method and precursor material; steam activation was significantly less expensive than phosphoric acid activation.

Agricultural by-products can serve as a source for activated carbon. Flax (Linum usitatissimum L.) is a crop that has supplied fiber (for linen textiles) and oil (linseed oil) for domestic and industrial use (Akin et al., 1996; Berglund, 2002; Bos, 2004; Domier, 1997; Miyake et al., 2003). Activated carbons have also been used in combination with zero-valent iron reactant and biodegradation (Bayer and Finkel, 2005; Nakano et al., 2000).

A variety of sources may be considered for activated carbon generation: coal, wood char, and agricultural by-products. Unlike coal and to some extent wood, agricultural by-products are abundant, low-cost and renewable. Many estimates exist on the amount of agricultural and forest resources that exist for use. In a recent report, it was estimated that 129 and 176 million dry tonnes are available for bioenergy and bioproducts from forestry and agriculture, respectively; and this could be increased substantially with different agricultural management practices (USDOE, 2005).

Flax (Linum usitatissimum L.) is a crop that has supplied fiber (for linen textiles) and oil (linseed oil) for domestic and industrial use (Akin et al., 1996; Berglund, 2002; Bos, 2004; Domier, 1997; Van Sumere, 1992). In order to obtain the fiber (which is contained in the stem) the material is retted, which separates the fibers from the other parts of the stem. The most common type of retting is dew-retting (Van Sumere, 1992) or the older warm water retting
method (Daenekindt, 2004). Both methods are based on a micro-
bial attack on parts of the materials in the stem that allow for eas-
er separation of the cellulose fibers. As the traditional methods
are microbial in nature, other direct enzymatic methods have also
been developed to make the process more consistent (Akin et al.,
2007). In all cases, the stem material that is left when the fibers
have been separated through retting is called shive, which is the
woody, lignified inner tissue of the stem. Total fiber (which in-
cludes short and long fiber) in flax is in the range of 31–37% of des-
eeded straw (Stephens, 1997) and straw represents about 74% of
the harvested material (Van Sumere, 1992). With an annual 2007
production of 5.9 million bushels (150,000 tonnes) seeds in the
US (USDA, 2008) and 989,000 tonnes in Canada (AAFC, 2008),
the amount of fiber-free flax shive potentially available in North Amer-
ica can be estimated at 2.1 million tonnes annually.

Cotton gin waste (or gin trash) is generated in the gin, where the
fibers are separated and the seeds are recovered. Cotton ginning is a
dry operation, relying on air flow, density and friction (Thomasson,
1990). The trash composition varies depending on the different
types of gins and harvesting practices, but it is generally in the form
of boll cover (burr), stems, and lint. Approximately 2 million tonnes
of cotton gin waste is generated each year (Holt et al., 2000).

The production of carbons from “woody” lignocellulosic materi-
als is a process where the material is pyrolyzed under an inert
atmosphere before it is activated (Lima et al., 2004). Sometimes
the activation is done in conjuction with pyrolysis, sometimes
in sequence. Steam activation is the most common method of pro-
ducing activated carbons, but acid activation, or carbon dioxide
activation has also been used (Johns et al., 1999; Toles et al.,
2000a,b; Wartelle and Marshall, 2001).

In this paper, we describe the performance of activated carbons
made via steam or phosphoric acid activation of cotton gin waste
or flax shive. The activated carbons were used to adsorb TCE from
water and vapor phases.

2. Methods

2.1. Materials

Flax shive was obtained after the processing of dew-retted and
enzyme-retted (Akin et al. 2007) flax stems from the US Depart-
ment of Agriculture Flax pilot plant, Clemson, SC. The shive was
milled through a Wiley mill (Type No. 1, Arthur H. Thomas Co.,
Philadelphia, PA) with a 2-mm mesh screen. Cotton (harvested
with a picker) gin waste was obtained from the US Department
of Agriculture Cropping Systems Research Laboratory, Lubbock,
TX. The gin waste was ground in a Retsch mill (Type SM2000/
835 upm; Kurt Retsch Gmbh, Haan, Germany) and sieved to retain
the 0.84–2 mm (No. 10-20 sieve) fraction for conversion to acti-
vated carbon.

Commercial carbons Norit C and Vapure 612 from Norit Amer-
icas, Inc. (Marshall, TX) and Calgon Filtrasorb 300 (Calgon Carbon,
Bay St. Louis, MS) were used for comparison purposes. The carbons
were used without further milling. Based on manufacturer’s infor-
mation, Norit C is a phosphoric acid-activated carbon used for adsorbing high molecular organics, Calgon Filtrasorb 300 (Calgon
F-300) is a bituminous coal-based carbon designated for use in
removing dissolved organic compounds in potable water, and Norit
Vapure 612 is recommended for removal of hydrocarbons from gas
streams.

2.2. Pyrolysis and activation

For steam activation, flax shive or cotton gin waste (100–
150 g) was placed in a porcelain evaporating dish (265 mm
diameter, CoorsTek, Golden, CO) and pyrolyzed in a high-temperature
furnace with retort (Lindberg, Type 51662-HR, Watertown, WI) for 1 h at 700 °C with continuous flow (1.6 L/min) of nitrogen
gas. The void volume of the furnace was approximately 22 L. Following the pyrolysis, the furnace temperature was in-
creased to 850 °C and the material was steam activated for 1.5 h by introducing water at a flow rate of 3 mL/min into the
nitrogen gas entering into the cavity of the furnace. After activa-
tion, the furnace contents were allowed to cool overnight with a
constant nitrogen gas flow (1.6 L/min). After cooling, the carbon
was washed with 0.1 M HCl at a ratio of approximately 100:1
(w/w, liquid:carbon) for 1 h, then washed over a No. 60 sieve
screen (0.25 mm opening) with deionized water to a neutral
pH, and finally oven dried at 80 °C.

For phosphoric activation, flax shive or cotton gin waste (100–
150 g) and phosphoric acid (30% by weight) were mixed in the
cornel evaporating dish at a 1:1 ratio of material to dilute
acid. The material was allowed to absorb the phosphoric acid
solution overnight before activation at 450 °C in the Lindberg fur-
nace with a continuous flow (1.6 L/min) of air. After activation,
the furnace was allowed to cool overnight with constant air flow
(1.6 L/min). The resulting carbon was washed five times in hot
water (90 °C) at a ratio of approximately 100:1 (w/w, water:car-
bon) and only the fraction above No. 60 sieve screen was re-
tained. The resulting carbon was oven dried at 80 °C.

Average particle size of the final experimental products was
determined using five standard sieves (0.25, 0.30, 0.43, 0.60, 0.84,
2.0, and 2.8 mm) and weighted average calculations.

2.3. Experimental methods

2.3.1. Liquid adsorption study

Single-point adsorption studies for feasibility screening pur-
poses were carried out in 40 mL glass vials using 0.01 g of activated
carbon and 20 mL of water containing TCE at a concentration of 25
or 35 mg/L. The vials were agitated for 24 h at room temperature
and the liquid was analyzed for TCE. In the isotherm studies, two select carbons were evaluated by varying the volume in 5 mL increments from 10 to 40 mL of a solu-
tion with 25 mg/L of TCE for Calgon F-300 and 35 mg/L of TCE for
steam activated carbon made from enzyme-retted flax shive. (The higher concentration of TCE for the flax shive carbon was to
account for the better performance of this carbon.) The carbon
weight in each vial was kept constant at 0.01 g. The samples were
evaluated after 24 h of mixing.

2.3.2. Vapor adsorption studies

For vapor adsorption studies, the activated carbon was placed
in a 300-μL vial insert (National Scientific Co., Rockwood, TN) en-
cased in a 15 mm circular ethylene vinyl acetate foam disc so
that the vial was suspended in the liquid. The foam disc with
the vial was placed into a 20 mL head-space analysis autoinjector
vial containing 10 mL of 100 mg/L of TCE in water and 4 g sodi-
um sulfate (Fig. 1). The sodium sulfate forced the TCE into
the head-space of the vial so that the volatile TCE could passively
be adsorbed by the carbon contained in the (insert) vial. After
24 h contact at room temperature (22–24 °C), the sample vials
used in the vapor phase experiments were analyzed without fur-
ther preparation. At these conditions, the relative humidity in the
head-space of the vials was estimated (Apelblat and Korin, 2002;
Liley et al., 1997) at 80%.

For adsorption isotherms of the two selected activated carbons
the amount of carbon was varied from 0.01 to 0.08 g, as the liquid
volume and TCE concentration were kept constant at 10 mL and
100 mg/L, respectively.
2.4. Analytical methods

Following contact of liquid (containing TCE) and activated carbons, a 10-mL aliquot was filtered using a 0.45-μm-pore-size syringe filter into a 20-mL sample vial for head-space analysis. Four grams of anhydrous sodium sulfate was added to saturate the solution and to drive the organic compounds into the head-space for solid-phase microextraction (SPME) analysis using a carboxen/methylpoly–siloxane/divinylbenzene SPME fiber (Supelco, Bellefonte, PA). The SPME fiber adsorbed the analytes for 15 min with agitation at 40°C using a CTC Combi PAL autoinjector (Leap Technologies, Carrboro, NC) on a Agilent Model 6890N gas chromatograph (GC) with a Model 5973N mass spectrophotometer (MS) detector (Agilent Technologies, Inc., Santa Clara, CA) to detect the TCE. A 30 m × 0.32 μm HP-5 ms [(5%-phenyl)-methylpolysiloxane] capillary column from Agilent Technologies was used in the GC. The temperature for the pulsed-splitless injector was 270°C. The oven temperature was held at 35°C for 5 min, ramped at 8°C/min, and held at 110°C for 2 min. Selective ion monitoring on the mass spectrometer detector (source held at 150°C and quadrupole at 106°C) was used to acquire area counts at 95 and 130 m/z. Calibration, using 5–6 standards was performed using known concentrations of TCE in water and the head-space analysis method and detection limits for TCE were 5 μg/L, which was similar to that of Poli et al. (2005).

In the case of measurement of vapor phase concentration in the air studies, and due to the high concentration in the vapor phase, the SPME fiber was manually exposed to the vial’s head-space (Fig. 1) for 30 s at room temperature before desorbing in the GC injector. Calibration of the head-space analysis method was done with known standard concentration solution of TCE in water (and salt). However, after the head-space of a calibration standard had been analyzed, the head-space was purged with a gentle stream of air for 10 s, recapped, and reanalyzed. Using this procedure, the TCE distribution between vapor and liquid in the standards could be calculated using the following equations:

\[
C_l = A_2C_0 / A_1 \\
C_v = (V_0C_0 - V_1C_1) / V_C
\]

where, \(C_l\), \(C_v\), and \(C_C\) are the concentrations (in μg/L) of TCE in the standard, the equilibrium liquid phase, and the equilibrium vapor phase, respectively; \(A_1\) and \(A_2\) are the area counts from gas chromatography analysis (see above) of unpurged and purged standards; and \(V_0\), \(V_1\), and \(V_C\) are the volumes of the standard, the liquid phase, and the vapor phase, respectively. These calculations then allowed for calibration curves to be established for both the equilibrium vapor and liquid phase concentrations as a function of the area.

Surface areas for the activated carbons were determined using a Quantachrome NOVA automated nitrogen gas adsorption system (Quantachrome Instruments, Boynton Beach, FL) that reported Brunauer–Emmett–Teller surface area and micropore (in pores of less than 2 nm diameter) volume measurements. Samples were run in duplicate.

2.5. Regression and statistical analysis

Regression curves for the isotherms were determined using the non-linear regression analysis feature of SigmaPlot 2002 for Windows (Version 8 by Systat Software, Inc., San Jose, CA) and the ANOVA variance analysis (\(P < 0.05\)) and correlation was done with Microsoft Excel 2003 (Richmond, WA) with post hoc Tukey Honest Significant Difference test equations (Walpole and Myers, 1989). In this manner, the data from individual activated carbons could be ranked into groups within which no significant difference could be statistically proven.

3. Results and discussion

The laboratory manufacture of washed activated carbons resulted in yields of 7.1–15.6% for steam and phosphoric acid activation, depending on the starting material (Table 1). These yields are lower than those obtained for some nut shell–based activated carbons (pecans, walnuts) but similar to those found for soft nut shell (almond) based activated carbons using steam activation under similar conditions (Toles et al., 2000a; Wilson et al., 2006). The phosphoric acid–activated carbons were manufactured at yields of approximately 12%, which are significantly lower than those reported for hardwood (Lima et al., 2004) and nut shells (Toles et al., 2000b; Ahmadna et al., 2004). The final average particle size for all the experimental carbons was 0.90 mm but phosphoric acid activation resulted in carbons with around 35% smaller particle size than its steam-activated counterparts. The surface areas for the laboratory carbons ranged from 530 to 923 m²/g, with steam activation being the most effective in generating surface area from the same starting raw material (Table 1). The commercial carbons used in this study had generally a higher surface area.

The feasibility studies with a variety of carbons and a single concentration of TCE in the liquid (or vapor) phase allowed for ranking of the carbon, which served as a guideline for which activated carbons to include in the more detailed isotherm studies. The feasibility studies were conducted in triplicate; while the isotherm studies were conducted in single experiments, which used a variety of liquid to solid ratios and initial TCE concentrations to cover as much of the isotherm range as possible for each carbon tested.

3.1. Studies in the aqueous phase

The results obtained when TCE in the liquid phase was contacted with activated carbon showed that the activated carbon
adsorbed TCE in the range of 30–50 mg/g of activated carbon (Fig. 2) under the conditions used. There was no significant difference in TCE adsorption among most of the carbons. Two carbons that performed slightly worse than the others: the commercial carbon (Calgon F-300) and the phosphoric activated carbon made from dew-retted flax shive. In general, the steam activated carbons made from agricultural by-products performed better than their phosphoric acid-activated counterparts. The correlation coefficient was –0.07 between specific surface area and adsorption capacity; thus, higher surface area in the carbons did not necessarily result in better adsorption of TCE.

In the isotherm studies, the best performing activated carbon as shown in Fig. 2 (steam activated carbon from enzyme-retted flax shive) was compared with the commercial carbon Calgon F-300. The results show that for most of the range of TCE concentrations, the capacity of the flax shive carbon was higher than that of the Calgon F-300 carbon. For example, Fig. 3 shows that at an equilibrium concentration of 4 mg/L of TCE in water, the adsorptive capacity was approximately 50 and 110 mg TCE/g of carbon for Calgon F-300 and the steam-activated flax shive carbon, respectively. At an equilibrium TCE concentration of 1 and 2 mg/L, the steam-activated flax shive carbon adsorbed 50 and 80 mg TCE/g of carbon, respectively (Fig. 3). Both sets of adsorption data were shown to be predicted by either Langmuir or Freundlich isotherm models, with correlation coefficients slightly better for Freundlich model (data not shown).

The studies conducted here compare well with other studies reported in the literature for steam-activated carbon. Karanfil and Dastgheib (2004) and Urano et al. (1991) showed that Calgon F-400 adsorbed approximately 100 mg of TCE/g of carbon and Sotelo et al. (2004) suggested that 250 mg of TCE/g of carbon (Norit GAC-1240) could be adsorbed at 4 mg/L of equilibrium TCE concentration. O’Brien and Stenzel (1984) showed that Calgon F-300 could adsorb 60 and 100 mg of TCE/g of carbon at equilibrium TCE concentration of 1 and 4 mg/L, respectively. While these studies noted higher capacities than in our studies, other studies by Yu and Chou (2000) found that 30 mg of TCE could be adsorbed onto 1 g of Calgon F-400 at an equilibrium TCE concentration of 1 mg/L; this is slightly lower than the values obtained in our studies at 1 mg/L of TCE (Fig. 3). Zytner (1992) predicted that 82 mg of TCE would be adsorbed onto Westvaco Nuclear activated carbon at an equilibrium concentration of 1 mg TCE/L. While it is difficult to compare results, it is clear that the values obtained in our studies are in general agreement with literature values.

3.2. Studies in the vapor phase

The results obtained when TCE was contacted with activated carbon in the vapor phase showed that the activated carbon adsorbed approximately 35 mg of TCE/g of activated carbon (Fig. 4) under the conditions used. There were no statistical differences between the carbons tested. The steam and phosphoric acid-activated carbons made from agricultural by-products performed equally well and were comparable with the commercial carbons.

In the isotherm studies, we again used steam activated carbon from enzyme-retted flax shive and compared TCE adsorption with the commercial carbon Norit Vapure. The results show that for most of the range of TCE concentrations, the capacity of the flax shive carbon was higher than that of the Norit Vapure. For example, Fig. 5 shows that at an equilibrium TCE concentration of 2 mg/L of air, the adsorptive capacity was approximately 50 and 130 mg TCE/g of carbon for Norit Vapure and the steam-activated flax shive carbon, respectively. At an equilibrium concentration of 1 mg/L, the adsorption capacity was 64 mg TCE/g of carbon for the steam-activated flax shive carbon. Both the isotherms followed a linear isotherm equation in the range of concentrations studied (Fig. 5).
The studies conducted here compare well with other studies reported in the literature for steam activated carbons. Miyake et al. (2003) found that activated carbon fibers adsorbed TCE, stripped from water, with different capacities depending on the relative humidity. At a TCE concentration of 2 mg/L of nitrogen, they observed equilibrium capacity of 220 mg TCE/g of carbon for an Adall A-20 carbon at 80% relative humidity. With a different carbon (Adall A-10), the equilibrium capacity was 40 mg TCE/g of carbon for relative humidity of 75%; the vapor phase concentration of TCE in this case was 0.86 mg/L. This data again shows that some activated carbon capacities reported in the literature are similar (some higher and some lower) to the capacities that are herein reported for novel activated carbons made from agricultural by-products.

3.3. Estimation of manufacturing cost of activated carbon from agricultural by-products

The costs of manufacturing activated carbon from flax shives and cotton gin waste are not known at this time; however the costs of producing activated carbons from nutshell shells using the phosphoric acid and steam activation have been estimated in the literature (Toles et al., 2000a,b). This production cost was approximately $1.50–4.30 per kg, depending on precursor material. For acid-activated carbons, the cost reported was $2.40–2.80 per kg with a yield of 38%. These cost estimations are preliminary in nature, and only take into account the difference in yield (compared with previously published costs) and do not include profit.

4. Conclusions

Activated carbons made from agricultural by-products such as flax shive and cotton gin waste performed as well or better compared to selected commercial activated carbons. Detailed isotherm studies suggested that steam-activated carbon from enzyme-retted flax shive outperformed different commercial carbons by a factor of two when used as an adsorbent for TCE in liquid or vapor phases. The capacity of the carbon in the liquid and vapor phases was similar (within the limitations of the method) at low equilibrium concentrations of TCE; however, as expected, the adsorption capacity in the vapor phase is higher than in the liquid phase at higher equilibrium concentrations. It should be noted that the vapor phase studies took place at high relative humidity (80%) and the loading capacity in the vapor phase is very dependent on humidity (Miyake et al., 2003). Activated carbon, especially from flax shive but also from cotton gin waste, provides an efficient adsorbent for TCE that can be produced from a low-cost, renewable agricultural by-product.

References

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