Evaluation of Nitrate Retention Additives for Developing Environmentally Friendly Manures

ABSTRACT

Activated carbon is a readily available material that can be added to fertilizers or manures to reduce nitrate nitrogen (NO_3-N) contamination of surface and near-surface groundwater. To test the nitrate adsorption performance of activated carbon, its absorbance was compared to that of used wall board (gypsum), sand, carbon, iron filings, wheat litter, wood litter, coffee grounds, bauxite residue and vermiculite using a nitrate ion selective electrode. Of these adsorbent candidates, only activated carbon exhibited a significant nitrate adsorption capacity.

A linear adsorption isotherm was observed ($r^2 = 0.975$) over the dosing range 0.77-6.1 mg NO_3-N/g activated carbon using nitrate standards. The adsorption capacity observed using neat standards was 0.69 mg NO_3-N/g carbon. The performance of activated carbon for adsorbing nitrate under simulated runoff conditions was evaluated for 10, 20, 30, 40 and 50 weight % mixtures of activated carbon with cow manure. The nitrate adsorption capacity observed for mixtures of activated carbon and cow manure was 0.47 mg NO_3-N/g carbon, which is 68% of the ideal adsorption capacity observed using neat standards. This shows that activated carbon can be added to cow manure to significantly reduce NO_3-N runoff to water supplies and create an environmentally friendly manure-based fertilizer.

INTRODUCTION

The availability of safe drinking water is a worldwide concern exacerbated by the effects of pollution, water-borne disease and increased consumption (Gleick, 1999). It is necessary to continue to develop effective, sustainable, accessible methods for treating water to allow safe re-use by living organisms.

Nitrate (NO_3^-) is a colorless, odorless and tasteless compound that is often applied to soil as a water soluble component of fertilizers and manures. Nitrate nitrogen (NO_3-N) is an essential component for plant growth that is often applied to crop plants in large quantities to sustain high yields. Unfortunately, NO_3-N is also considered a potential pollutant by the Environmental Protection Agency (EPA).

Nitrate can cause health problems and environmental hazards when excess NO_3-N runoff collects in discharges and streams or leaches into near-surface ground water. Examples of these hazards include methemoglobinemia ("blue baby" syndrome") and oxygen deficient "dead-zones" due to algae blooms in rivers, lakes and oceans (Johnson, et. al., 2000). Nitrate concentration can be expressed as either NO_3^- or NO_3-N. The EPA maximum contaminant level for NO_3^- in drinking water is 10 ppm NO_3-N or 45 ppm NO_3^- (Federal Register, 1975).

The goals of this project were to:

1) comparatively evaluate readily available, inexpensive materials that could be added to manures, fertilizers or soil to reduce the loss rate of NO_3-N into near-surface groundwater during rainfall or watering of fertilized fields
2) characterize the ideal nitrate adsorption performance of the best candidate using nitrate standard solutions, and
3) evaluate the performance of the best nitrate adsorption candidate under "simulated runoff" conditions, using cow manure as the nitrate source.

MATERIALS AND METHODS

Samples of cow manure, soil, wall board, sand, iron powder, bauxite residue, wood litter, wheat litter, coffee grounds and activated carbon were dried at 110° C for several hours. Any large or "clumped" materials (used wall board, soil, cow manure, etc.) were ground to powders to allow for homogeneous sampling.

A nitrate ion selective electrode (ISE) was calibrated using 1-500 ppm calibration standards as-is and after mixing each standard (10 ml:10 ml) with nitrate interference suppressor (NIS) solution. The nitrate ISE response (millivolts) versus the natural logarithm of NO_3-N concentration is shown in Figure 1. All nitrate concentrations shown in this report are in units of nitrate nitrogen (NO_3-N).

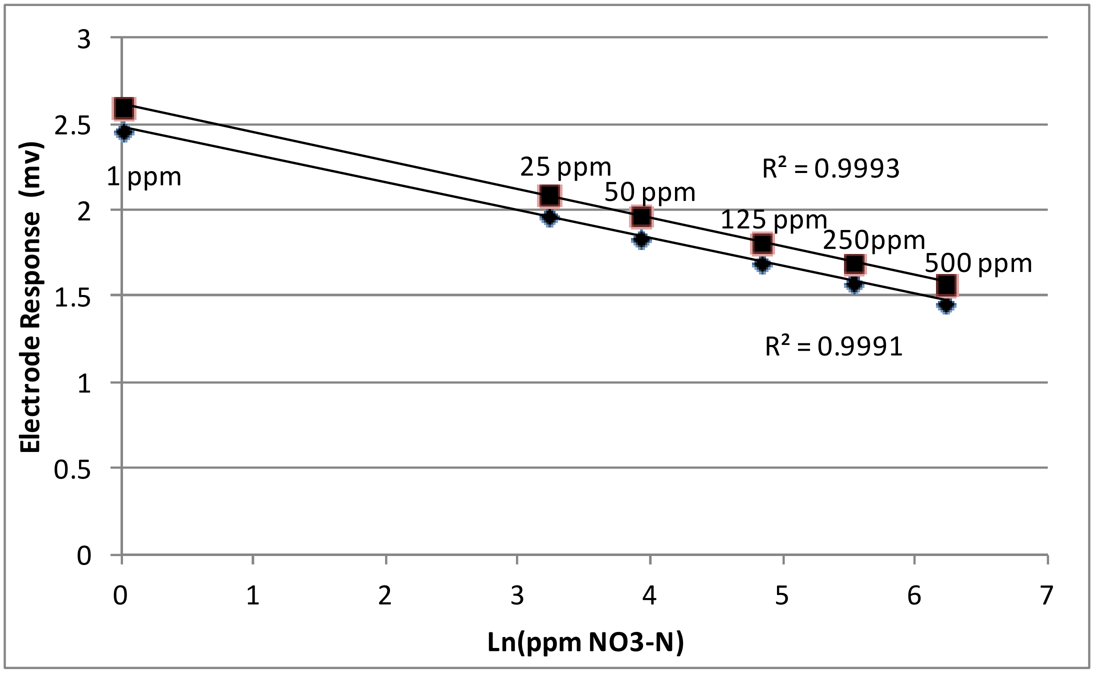

Figure 1. Nitrate ISE response (mV) versus Ln(ppm NO_3-N) for neat nitrate standards (diamonds) and after mixing the nitrate standards (50%) with nitrate ion suppressor solution (boxes).

As shown in Figure 1, the nitrate ISE response in millivolts (mV) shows a negative, linear correlation ($r^2>0.999$) to the natural logarithm of NO_3-N concentration over the range 1-500 ppm. As expected, the nitrate standards mixed with NIS gave higher ISE mV readings for given NO_3-N standard concentrations, since these samples are diluted by mixing with NIS, compared to the neat (no NIS added) nitrate standards. Calibration equations based on the data shown in Figure 1 were used to calculate NO_3-N concentrations for all nitrate ISE data shown in this report.

Nitrate ISEs are known to exhibit responses to a number of interfering ions (Wilhelm, et. al., 2000; Willard, et. al., 1974) NIS (nitrate interference suppressor) was used (10 ml sample:10 ml NIS) to prevent these interferences from causing errors in the nitrate ISE response. The composition of the NIS solution used in this report, as well as the interferences addressed by each component, is listed in Table 1.

Table 1. Composition of Nitrate Ion Suppressor Solution.

Component	Chemical Formula	Purpose
De-ionized water	H_2O	Carrier solution
Aluminum Sulfate	$Al_2(SO_4)_3$	Prevents interference from organic ions
Silver Sulfate	$Ag_2(SO_4)_3$	Prevents interference from halogens & sulfide ions
Sulfamic Acid	H_2NSO_3H	Converts nitrite (NO_2^-) to nitrate (NO_3^-)
Boric Acid	H_3BO_3	Prevents interference from carbonate & bicarbonate ions

The experimental procedures used to generate the performance data shown in this report are summarized as follows:

Known weights of cow manure were placed in labeled beakers with 50 ml of deionized water and stirred for two hours to test the nitrate release behavior of as-received cow manure.

Known weights of each nitrate adsorbent candidate were placed in labeled beakers with 50 ml of 49 ppm nitrate standard and stirred for two hours to compare nitrate adsorption performance and identify the adsorbent candidate with the highest adsorption capacity. The NO_3-N concentrations were measured for the adsorbent candidate test samples as-is and after mixing samples of each (10 ml:10 ml) with nitrate interference suppressor solution.

Samples composed of two grams of activated carbon and two grams of cow manure were placed in labeled beakers with 50 ml of deionized water, and the NO_3-N concentration was measured at varying times to determine the performance of activated carbon mixtures for reducing free nitrate concentration as a function of time.

Varying weights of activated carbon were placed in labeled beakers along with 50 ml of NO_3-N standard and stirred for more than 3 hours prior to measuring dissolved NO_3-N concentration. This was done to evaluate the impact of the activated carbon to total nitrate ratio on the adsorption capacity of activated carbon (adsorption isotherm) under ideal simulated runoff conditions.

Varying weights of activated carbon were mixed with 2 gram cow manure in labeled beakers (along with 50 ml de-ionized water) and stirred for more than 3 hours prior to measuring the dissolved NO_3-N concentration. These measurements were performed in order to evaluate the effectiveness of varying carbon/manure loadings for reducing free nitrate concentration under simulated actual-use runoff conditions.

A nitrate ISE was connected to a Vernier LabPro data logger and used to make concentration measurements of 20 ml sample volumes in labeled vials. All data collection was performed using a notebook computer connected to the LabPro. All ISE measurements were performed on samples either “as-is” or as 50:50 (10 ml:10 ml) mixtures with NIS.

As noted above, 10 nitrate adsorbent candidates were evaluated in this study. Most of these adsorbent candidates were selected based on their use as soil amendments for improving the physical properties of soil (Brady and Weil, 2007; Chirenje and Ma, 2002; Davis and Wilson, 2005). Vermiculite, sand and wallboard were all purchased from a local building supply store. Wood litter, wheat litter and activated carbon were all purchased from a local pet store. Iron filings were obtained from a local scrap metal recycler. Clay soil was dug from a local yard. Bauxite residue, a waste product from the refining of alumina from bauxite ore, was donated by Alcoa. All samples were prepared as dried fine powders prior to analysis to allow for homogenous sampling.

The fixed parameters in this study were:

- Total solution volume of test samples (50 ml)
- Sample weights (adsorbent or manure)
- Sample stirring rate and time, and
- Nitrate concentrations (when using prepared standard solutions).

The variable parameters in this study were:

- Nitrate adsorbent candidates
- Nitrate adsorption rate and capacity
- Sample homogeneity, and
- Nitrate ion selective electrode response.

RESULTS AND DISCUSSION

Manure Nitrate Release Behavior

Cow manure samples (0, 1, 2 or 3 grams) were mixed with 50 ml deionized water and stirred in labeled beakers for several hours. 10 ml of each sample was mixed with 10 ml of NIS, and the NO_3-N concentration was measured using a nitrate ISE. The NO_3-N concentrations observed for these samples are plotted in Figure 2. The cow manure caused increased dissolved nitrate concentrations in linear proportion to the amount of manure mixed with water (simulated runoff). As shown in Figure 2, one gram of cow manure can release enough nitrate to cause the NO_3-N concentration in 50 ml of water to exceed the EPA maximum contaminant level for NO_3-N (10 ppm).

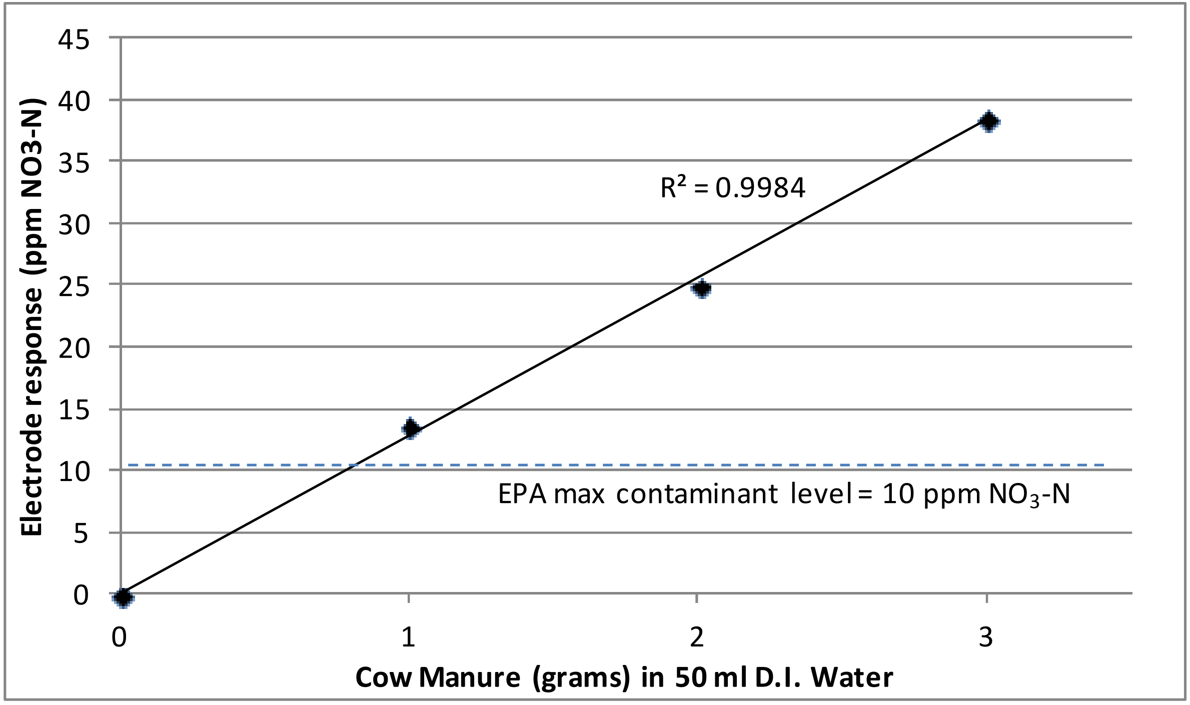

Figure 2. NO_3-N concentrations in 50 ml D.I. water mixed with varying weights of manure.

Adsorbent Candidate Performance Screening

Four grams each of 10 adsorbent candidate materials (described above) were mixed with 50 ml of NO_3-N standard solution (49 ppm NO_3-N) and stirred in labeled beakers for several hours and then allowed to sit unstirred for one hour. Nitrate ISE measurements were performed on 15 ml of untreated supernatant liquid from each adsorbent test, as indicated by the left bars in Figure 3. Three 10 ml samples of supernatant from each adsorbent candidate test beaker were also mixed with 10 ml NIS and the ISE measurement was repeated, as indicated by the right bars in Figure 3. The dashed line in Figure 3 indicates the initial 49 ppm NO_3-N concentration of each test solution. The error bars shown in Figure 3 for the ISE treated NO_3-N data represent $\pm$3 standard deviations (s.d.).

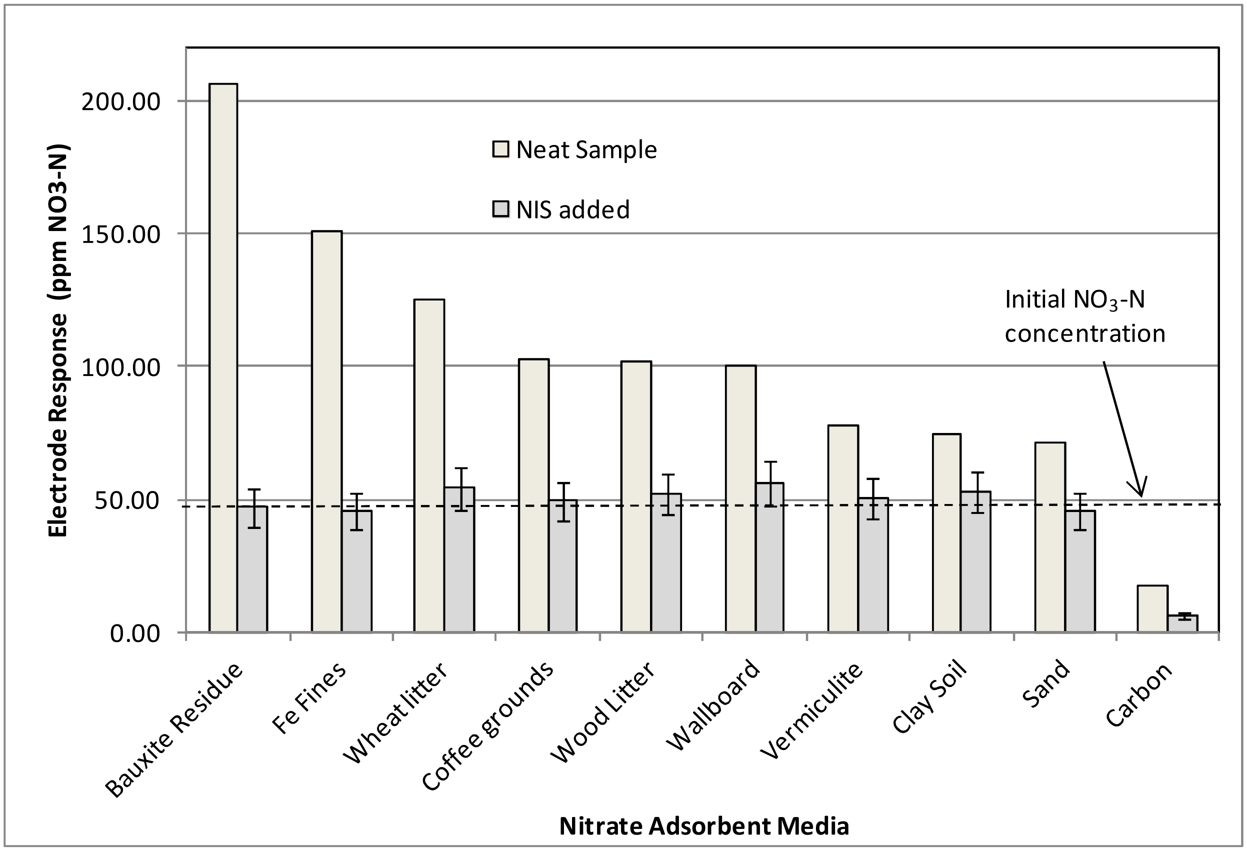

Figure 3. Nitrate adsorption candidate performance screening data. Light (right) bars indicate data from neat samples. Darker (left) bars indicate data from NIS-treated supernatant samples.

The data shown in Figure support several observations, listed below.

1) The untreated supernatant samples all gave higher “apparent” NO_3-N concentrations compared to the NIS treated samples.
2) The “apparent” NO_3-N concentrations observed for the untreated supernatant samples suggest that NO_3-N is released into the test solution from nine of the adsorption candidates.
3) The data observed for the NIS treated supernatant samples indicate that five candidates (bauxite residue, Fe fines, coffee grounds, vermiculite and sand) do not exhibit any significant effect on NO_3-N concentration, while wheat litter, wood litter, wallboard and clay soil, may release NO_3-N to the test solutions.

4) The only adsorbent candidate that exhibited significant nitrate adsorption capacity was activated carbon.

The higher “apparent” NO_3-N concentrations observed for the neat supernatant samples shown in Figure 3 suggest that NO_3-N was actually released into solution by all of the adsorbent candidates, except activated carbon. This “apparent” behavior is not possible, since adsorbents such as bauxite residue, Fe fines, sand, and vermiculite do not contain any nitrate. The high “apparent” NO_3-N concentrations observed from ISE measurements of neat solutions were due to interfering ions (see Table 1) that caused false positive responses from the nitrate ISE.

The NIS treated supernatant data shown in Figure 3 indicates that the NO_3-N concentrations are effectively unchanged (within 2% of initial concentration) for bauxite residue, Fe fines, coffee grounds, vermiculite and sand. Wheat litter, wood litter, wallboard and clay soil appear to release small amounts of NO_3-N to the test solutions. All of these four adsorbent candidates may contain nitrate. Wheat litter and wood litter are organic-based adsorbents; the soil sample likely contained adsorbed organic material and the wallboard may have contained nitrate-based chemicals in the paper facing of the wallboard.

The principal conclusion from the data shown in Figure 3 is that only activated carbon showed significant nitrate adsorption capacity. It is important to note that all NO_3-N data shown in the remainder of this study are from samples that were mixed with NIS to prevent interfering ions from affecting the nitrate ISE response.

Method Precision Error Estimation

Method precision error due to sample pipetting and ISE measurement repeatability was estimated by pipetting 10 ml of a prepared 83 ppm NO_3-N standard solution and 10 ml of NIS solution into a plastic vial, mixing the solution by shaking, then measuring the NO_3-N concentration using a nitrate ISE. This sample preparation procedure was independently repeated five times. The measurement data is shown in Table 2. The relative standard deviation error (RSD) observed for sampling (pipetting) and nitrate ISE measurement error was 2.69%.

Table 2. Pipetting and ISE Measurement Error Estimation Data.

Sample	mV	ppm NO3-N
1	1.768	81.94
2	1.758	87.12
3	1.769	81.43
4	1.76	82.96
5	1.765	83.47
average	1.76	83.36
std. dev.	0.0056	2.24
RSD (%)	0.32	2.69

The combined effect of pipetting, ISE measurement and sample homogeneity was estimated by preparing five independent samples by:

1) placing 2 grams of cow manure and 50 ml deionized water in labeled beakers,

2) stirring the solutions with a magnetic stirrer for 3 hours,
3) allowing the samples to sit unstirred for one hour,
4) pipetting 10 ml of supernatant from each beaker into labeled plastic vials with 10 ml NIS solution, mixing the solutions by shaking the vials, then
5) measuring the NO_3-N concentration in each sample vial using the nitrate ISE.

The data from the experiment described above is listed in Table 3. The relative standard deviation observed from the data in Table 3 was 5.07%. The data in Table 3 indicate that known concentrations of NO_3-N can be prepared from samples of cow manure mixed with deionized water with a precision (1 RSD) of ±5.07%.

Table 3. Pipetting, Sample Homogeneity and ISE Measurement Error Estimation Data.

Sample	mV	ppm NO3-N
1	2.095	21.2
2	2.075	24.06
3	2.090	21.91
4	2.089	22.01
5	2.081	23.13
average	2.09	22.30
std. dev.	0.0086	1.13
RSD (%)	0.41	5.07

Time Dependence of Activated Carbon Nitrate Adsorption from Simulated Cow Manure Runoff

Eight separate 2 gram samples of cow manure were mixed with 2 grams of activated carbon and 50 ml of deionized water in labeled beakers and placed on magnetic stirrers. Supernatant samples (10 ml) were pipetted from each beaker at specific times, ranging from 10 minutes to 240 minutes. Only one sample was taken from each beaker. The NO_3-N concentrations measured for each mixing time are shown in Figure 4, where the error bars represent ±3 standard deviations.

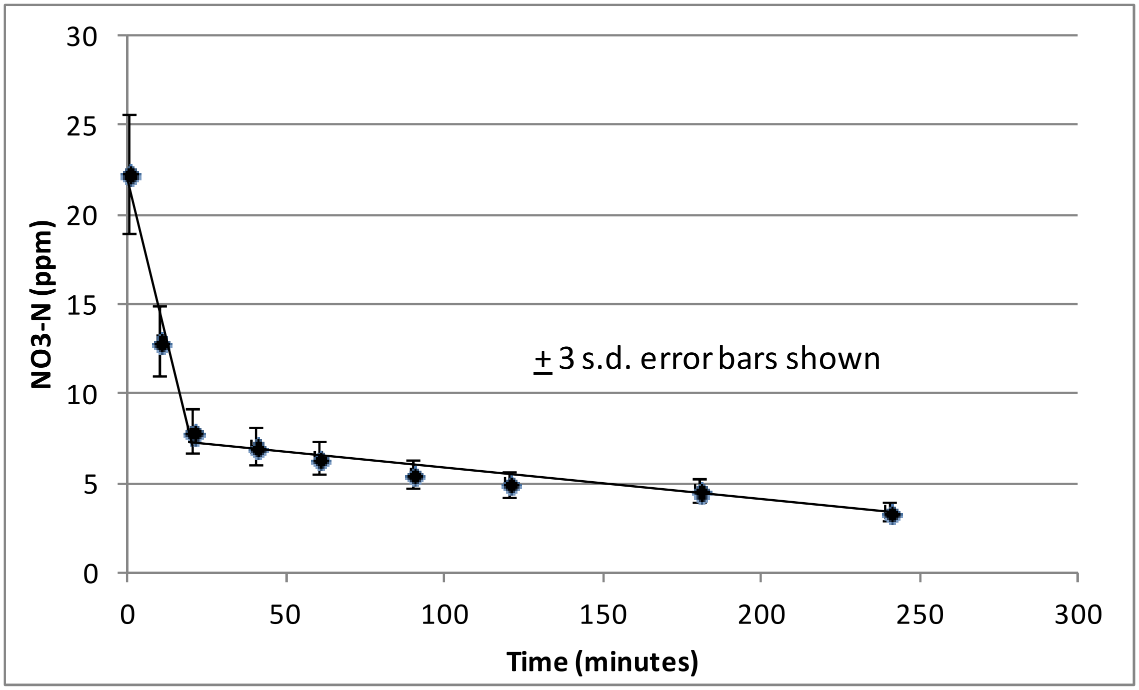

Figure 4. Time dependence of cow manure-based NO_3-N adsorption by activated carbon.

The NO_3-N concentration data shown in Figure 4 shows two distinct time-dependent adsorption rate behaviors. Over 75% of the total nitrate adsorption occurred rapidly over the first 20 minutes of mixing, followed by much slower nitrate adsorption over the next 3.5 hours. The data shown in Figure 4 clearly indicate that activated carbon is capable of rapidly adsorbing nitrate from solution to ~ 75% of total adsorption capacity, as shown by the first 20 minutes of mixing time, and will continue to slowly adsorb nitrate, over the remaining 25% of the adsorption capacity.

Nitrate Adsorption Isotherm of Activated Carbon

The ideal nitrate adsorption capacity of activated carbon was evaluated by placing varying weights (0.5, 1, 2, 3 and 4 g) of activated carbon in 50 ml of 62 ppm NO_3-N standard solution (62 mg NO_3-N /L * 0.050 L = 3.10 mg total NO_3-N) in labeled beakers, stirring for 3 hours, then measuring NO_3-N concentrations. This test procedure allows for the measurement of the nitrate adsorption capacity of activated carbon at different adsorbent to nitrate concentrations (activated carbon dosing levels), as shown in Figure 5, where the error bars represent ±3 standard deviations.

The NO_3-N adsorption capacity of activated carbon (mg NO_3-N/g activated carbon) increased in linear proportion ($r^2 = 0.975$) to the ratio of total dissolved NO_3-N (mg) to the total mass of added activated carbon (g). In other words, as the dosing level of activated carbon was reduced, the observed adsorption capacity of the activated carbon increased. The equation of the line for the data in Figure 5 allows for calculation of the expected NO_3-N adsorption capacity of activated carbon as a function of dosing level (mg total NO_3-N/g activated carbon).

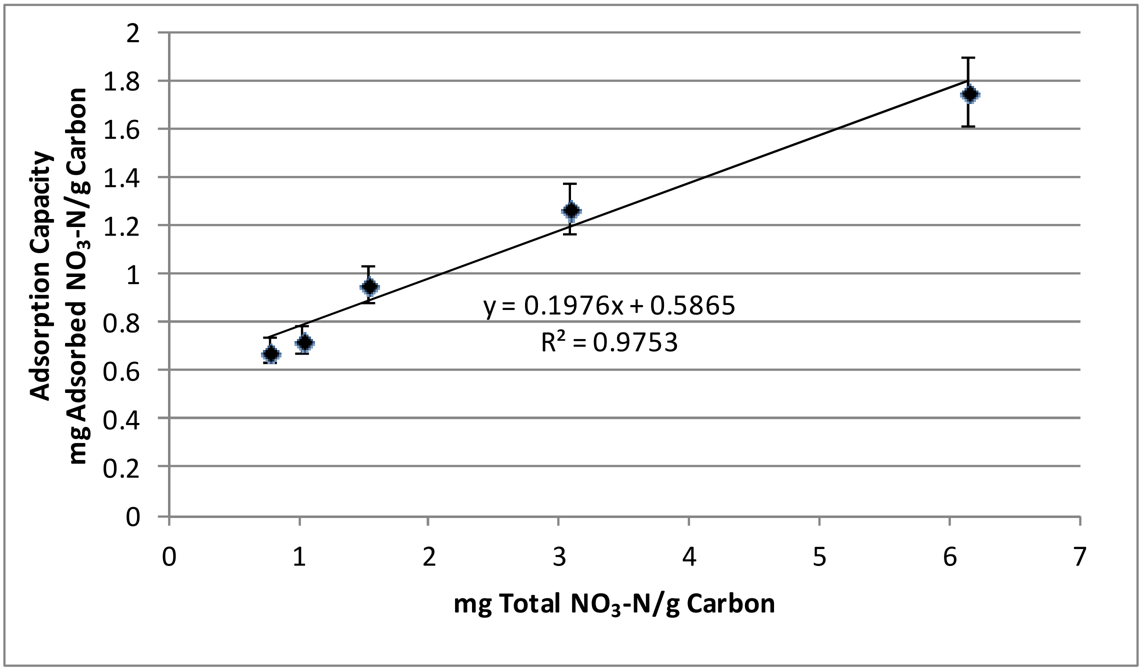

Figure 5. The NO_3-N adsorption isotherm for activated carbon.

Dosing Ratio Dependence of Activated Carbon Nitrate Adsorption from Cow Manure Runoff
The impact of the activated carbon dosing level (or mixing ratio) on simulated cow manure-based NO_3-N runoff was evaluated in order to determine optimum dosing conditions. Five separate sample conditions were studied, where each condition had a constant cow manure load (2 g) in 50 ml of deionized water. Each test condition, as represented by the bars in Figure 6, had a different activated carbon dosing level, ranging from 10, 20, 30, 40 and 50 weight %, relative to the weight of cow manure.

The upper horizontal dashed line shown in Figure 6 indicates the dissolved NO_3-N concentration (22.3 ppm) if no activated carbon was added to the test samples (see also Table 3). The NO_3-N concentration data shown in Figure 6 indicates that dissolved NO_3-N concentration is reduced in linear proportion to weight % activated carbon, over the range 10-30 weight % activated carbon to cow manure. Higher activated carbon dosages (>30 weight %) did not significantly reduce NO_3-N concentration in simulated runoff. It is important to note that 30 weight % loading of activated carbon reduces the NO_3-N concentration in simulated runoff to approximately half the EPA maximum contaminant limit (for NO_3-N) of 10 ppm, as indicated by the lower horizontal dashed line shown in Figure 6.

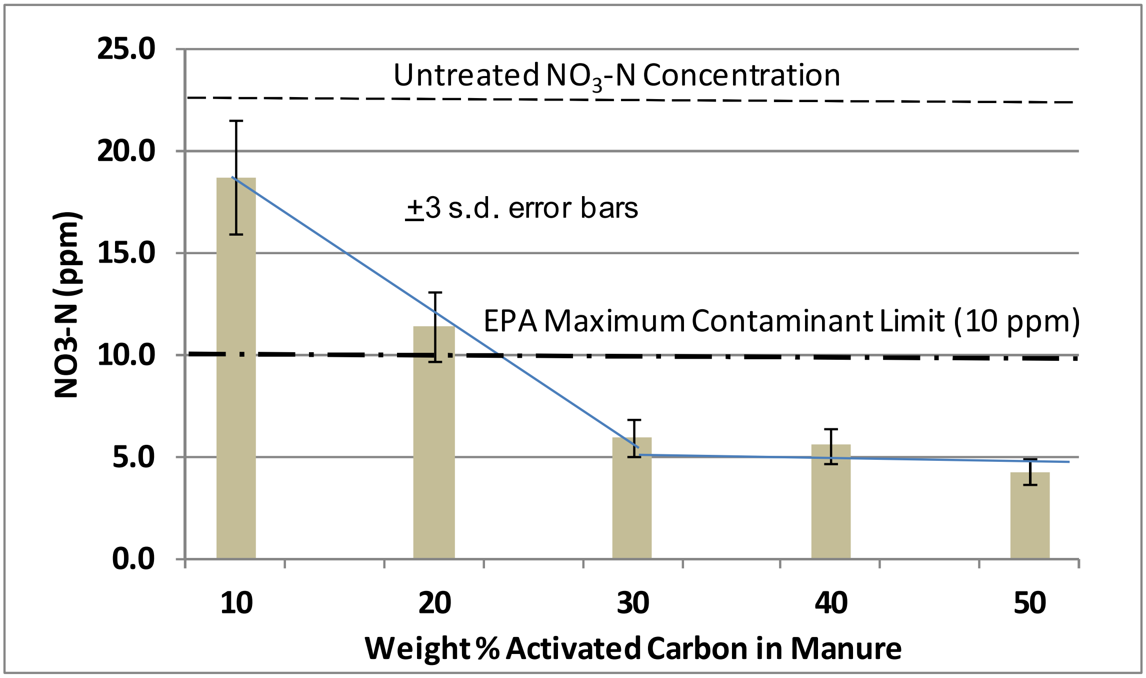

Figure 6. Dosing dependence of cow manure-based NO_3-N adsorption by activated carbon.

Nitrate Adsorption Capacities for Activated Carbon from Ideal and Cow Manure Based Runoff

The NO_3-N adsorption capacity of activated carbon under ideal runoff conditions can be calculated from the equation of the line of best fit in Figure 5. Using this equation, a nitrate adsorption capacity of 0.69 mg NO_3-N/g activated carbon is calculated under ideal runoff conditions for a loading level of 1.12 mg NO_3-N (50 ml of 22.3 ppm NO_3-N) to 2 grams activated carbon.

An activated carbon adsorption capacity of 0.47 mg NO_3-N/g activated carbon was observed for cow manure-based NO_3-N simulated runoff, as calculated from the data shown in Figure 6, where the total nitrate load ratio was 1.12 mg NO_3-N (50 ml of 22.3 ppm NO_3-N) to 2 grams activated carbon, the same conditions employed for the "ideal runoff" example discussed above.

The nitrate adsorption capacity observed for activated carbon in the cow manure test case was 68% of the adsorption capacity observed for the ideal (nitrate in deionized water) test case. The adsorption capacity reduction observed in the cow manure test case (relative to ideal) may be due to competitive adsorption from other ions released into solution from the cow manure under simulated runoff conditions.

CONCLUSIONS

The purpose of this project was to comparatively identify and characterize the adsorption performance of a readily available, low-cost material that could be added to manures, fertilizers or soil to reduce the loss rate of NO_3-N into near-surface groundwater during rainfall or irrigation.

The data obtained in the study show that clay soil, bauxite residue, wheat litter, wood litter, coffee grounds, sand, iron filings, wall board, and vermiculte have no significant capacity for adsorbing nitrate from solution.

Activated carbon can be added to cow manure to reduce the runoff nitrate concentration in linear proportion to the weight ratio (weight %) of added carbon, up to 30 weight %. The nitrate adsorption capacity observed for mixtures of activated carbon and cow manure was 0.47 mg NO_3-N/g carbon, which is 68% of the ideal adsorption capacity observed using neat nitrate standards.

A mixture of activated carbon (30 mass %) in cow manure can be used to increase nitrate retention and reduce free nitrate concentrations in runoff from fertilized fields.

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