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RESEARCH ARTICLE

Carbon source screening for nitrate remediation in permeable reactive barrier: Ion chromatography technique

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Abstract

In heterotrophic denitrification process, the integrity of carbon source within the gate of permeable reactive barrier(PRB) is as important as the remediation process itself. Problems of early depreciation rate of the electron source and pollution swapping have been reported to be amongst the recalcitrant factors. In an attempt to identify a new carbon source that can address some of the above mentioned problems, multi layer extracts of selected seed materials (Moringa Oleifera, Tamarind and Date seed) were subjected to ion chromatography screening for identification of denitrification active anion and antagonistic radicals. The results revealed that Moringa Oleifera seed cover had the highest sulphate content while Tamarind seed had the highest chloride content with multiple untagged peaks within the 3-6 min retention time region. The Date seed was found to be the most suitable on account of it's less anion radicals and slow rate of water absorption. The ultrasonic-aided batch analysis for adsorption measurement carried out on the the seeds revealed minor adsorption capacity (15%) for nitrate. It is recommended that the Date seed should be combined with fast degradable carbon substrate for effective exploitation in heterotrophic denitrification.

Keywords: Remediation, denitrification, permeable reactive barrier, date seed

INTRODUCTION

Permeable reactive barrier (PRB) are designed structures placed underground for the remediation of polluted shallow ground water (Thiruvenkatachari et al, 2008). The technology has been receiving attention on account of its effectiveness (Phillips D.H., 2009) and less maintenance requirement (Careghini et al.,2013; McGovern et al.,2002). This has been achieved through series of laboratory and field research, qualifying the technique to a level of most accepted in-situ remediation technology(Obiri-Nyako et al.,2014). Amongst the different approaches, such as chemical, biological and physical methods of remediation, biological method has been the most widely used (Lito et al., 2012). This is because of the microbe-aided self attenuating capacity and lower level of pollution swapping. Indigenous microorganisms are often utilized to break down the target pollutant while they feed on their substrate for their metabolic process. Examples are bioremediation of halogenated compounds (Samperini et al., 1992), petroleum compound (Gogoi et al. 2003; Maila and Cloete 2004) and nitrate remediation (Liu et al. 2014; Della Rocca et al. 2006)

The need for continuos supply of electron donors to ensure active participation of microbes in the remediation process presents a challenge to the requirement of longevity of the remediation system (Pu et al,. 2014). Research efforts aimed at reconciling the conflicting advantages of easy degradable carbon source and slowly degradable ones provide useful informations. For example, when ethanol and glucose were subjected to microbial activity, ethanol (having easy degradable carbon) was preferntially degraded (Jeris et al., 1974). Also, citrate/ Acetate was degraded in preference to glucose (Yang et al., 2012). At the expense of longevity, the easy degradable carbon source has the advantages of faster reaction rate(Isaac and Henze, 1995), shorter resident time and shorter gate length (Yang et al., 2012). While the slowly degradable carbon source lacks the aforementioned advantages, it posses the much needed longer life span. Hence, the need for the continuous presence of the reactive materials for the microbes to strive, presents a limiting factor to the process (McGovern et al.,2002). In field application, the reactive materials are placed in a gate or sheet of the PRB to serve as the electron donors for either heterotrophic or autotrophic denitrification respectively (Della Rocca, 2006).

Previous researches used a number of organic based gate materials comprising of synthetic and natural materials. The synthetic materials include methanol, glucose and acetate (Pan et al.,2013; Yang et al., 2012) while the natural ones include pine bark, saw dust and leaf compost (Huang et al,. 2015; Schipper, 2000; Robertson et al., 2000). Also, a number of inorganic source of electron donors (in autotrophic processes) include Sulphur (Liu et al., 2009; Sahinkaya et al., 2011), iron (Yu et al., 2006; Biswas and Bose, 2005) and Ion sulfide and pyrite (Haaejer, 2007). In most of the sources mentioned above, a setback of either pollution swapping or fast consumption of the electron donors (gate materials) is experienced or ignored. This call for the need to screen the reactive materials for the presence of analytes in remediation, competing radicals or objectionable by-products of decomposition (Yang et al,. 2012). The present work screened three seeds (Moringa Oleifera seed, Tamarind seed and Date seed) for the presence of the analyte (NO3-) and objectionable radical using Ion chromatography (IC). Since the materials are expected to be used in ground water remediation, their extraction was done in aquous region. Ion Chromatography analysis is used because its fastness in aquous medium.

EXPERIMENTAL

Materials

The eluents, consisting of 0.5M $NaHCO_3$ and 0.5M $NaCO_3$, the certified reference material (Sigma-Aldrich) and analar grade KNO_3 (Fisher Scientific) were used. The extraction and analysis were carried out with the help of ultrasonic machine, digital multi-use lab shaker, weighing balance and Dionex 1100 IC.

Extraction methods

In order to separate the seeds based on its outer and inner layer content, the seeds were partitioned into three parts -outer seed coat, middle seed coat and cotyledon. Decortification aimed at removing the fiber-saturated content was achieved through physical process of scrapping the coat of the seed with a sharp blade.

Two extraction methods were employed - the ultrasonic and agitation extraction method. In both methods, ground samples of the seeds were placed in water for three days respectively. On the fourth and fifth days, the seeds were removed and weighed untill a near constant weight was obtained. This was to assess the supersaturation threshold of the seed (absorption potential). 2g of the seeds in 20ml of water was subjected to ultrasonic extraction at operating frequency of 40kHz for 30min. The samples for the digital multi lab user shaker were agitated at 570rpm for 30min (Baharvand et al., 2014). Physical observations of the extracts and pH measurements were made.

Nitrate adsorption capacity of date seed and tamarind seed was measured by introducing 25ml of 100ppm KNO_3 solution into 50ml flask containing 25ml of water and 2g of the seed. The extraction procedure was then followed before the absorption measurement using IC.

To measure the effect of variation of pH on adsorption capacity, 0.5M HCl and 0.5M KOH was introduced into two separate date seed extraction medium at the ratio of 1:20 (v/v).the resultatnt extract was then taken to IC for analysis

Ion Chromatography (IC) analysis

The IC (Dionex 1100) was operated in accordance with the manufacturers guidelines. The eluent was prepared by mixing 8ml of 0.5M $NaCO_3$ with 1m of 0.1M $NaHCO_3$ into 500ml-volumetric flask and filled to the mark with deionized water. A serial dilution of certified reference material was made to a concentrations of 0.2, 0.4 and 0.6 ppm respectively. Injection of 1ml (DW), std1 , std2 and std3 through 0.2µm filter was made at a program time of 15min . The program time was limited to 15min because the highest retention time of the analyte of interest (NO_3^-, NO_2^- and SO_4^{-2}) is less than 15 min. Fig 1. Shows the schematic diagram of steps for screening date seed.

RESULTS AND DISCUSSION

Physical properties of the seed's fractions and extracts

The observed physical properties of the Tamarind seed revealed a more pigmented outer fraction and extracts of the seed cover with less cohesive texture in the cotyledon. The pH values of the Tamarind extract fractions were 8.87, 8.27 and 6.78 for outer, middle and inner extracts respectively. The Date seed showed more uniform distribution of hard texture across the layers and gave a pH distribution of 6.2, 5.4 and 5.7 for the three fractions respectively. The Moringa seed had more layers with the outer one being lighter and the cotyledone dampened with moisture and air sacs. The pH of Moringa seeds were 8.96, 9.2 and 6.69 for the three fractions respectively. A noticeable odour was perceived in Moringa seed extracts which intensified to rotten egg smell akin to hydrogen sulphide after two days. The water absorption potential measured indicated that the date seed had the least followed by tamarind and moringa seed. The moringa seed however tends to lose its texture with time, slowly dissolving away in the aqueous solution.

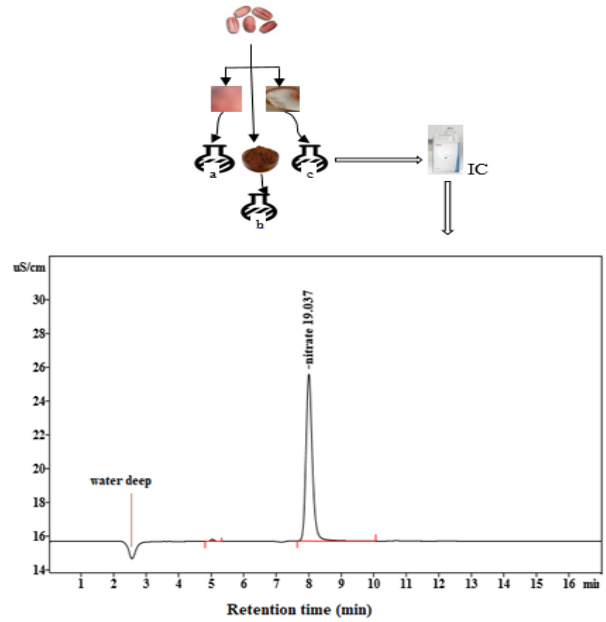

Fig. 1. Schematic steps in screening date seed. (a) Coat of the seed, (b) middle coat and (c) cotylydone.

IC Response to extraction Methods

The results of the IC run for the two extraction methods indicated that the ultrasonic-aided extraction had better extraction results than the agitation-aided method. This is due to the recovery of higher value (concentration) of the analyte (NO_3^-). Absorption capacity of the date seed and tamarind seed for NO_3^- solution was found to be within (15%) and the spectral distribution of anions indicated more objectionable products in tamarind and moringa seed than in date seed (Fig. 2).

Evaluation of the anions distribution across the layers

It was observed that though, tamarind (Fig 2(c)) has low nitrate value of 0.124ppm, it has high sulphate content 26.95ppm. Depending on the concentration and condition, chloride is reported to either be insignificant in influencing denitrification (Lancaster **et al.**, 2016) or advantageous (Azan and Muller, 2003). Despite this, the tamarind seed is considered inappropriate for the purpose due to possible competition of NO_3^- with the oxygen bearing anions(Shrer et al.,2000). The spectra of tamarind extract is also full of many untagged peaks) between 3-6 min. Peaks within this range indicates presence of organic acids in the medium (Jim Crol, 2000).

The result in (Fig 2(b)) indicates that moringa Oleifera has low nitrate value (0.122 ppm), moderate chloride (3.723 ppm) across the layers and medium sulphate value (2.927 ppm) on the cover. Considering the assertion of Pu ***et al***.,(2014), sulphur containing rocks are useful in heterotrophic denitrification. On this note, it is recommended that, the cotyledon of the seed can be exploited for prompt heterotrophic denitrification. The result in Fig 2(a) shows less objectionable anion content of dates seed and the observed low water absorption capacity of the seed is expected to ensure slow decomposition process. The slow decomposition of the dates seed will prolong its life span. Also, previous research that revealed high percentage of carbohydrate 72% in the dates seed (Nehdi,2010) indicates the presence of a condenced form of carbohydrate. The advantage of this situation is that the microrganism will be provided with slow, but steady supply of carbon source (Streitelmeier et al. 2001).

As indicated in Fig 3.(e), the NO3- absorption capacity of dates seed is not significant. The seed reduces only 15% of the original 50 ppm NO3- solution.. However, identification of NO2- peak in the chromatogramm suggest possible interconversion of NO3- to NO2- in denitrification.

Fig. 3 (f) shows the efect of lowering the pH of the extracts on the IC response (detection). Lower pH tends to affect the respose as well as the elution pattern of the the Ion Chromatography. First, the retention time shifted backward, eluting chloride earlier than its time. Secondly, lowering the pH supresses the release of chlorides in the seed and generate a peak within the phosphate detection region. This suggests that phosphates are sequesttrated under acidic medium. On the other hand, adjusting the Ph of the medium to basic side supports the release of chloride within the seed . Also the water deep peak becomes very prominent in basic medium. However, it is observed that neither basic nor acidic medium enhances the NO3- adsorption/extraction capacityof the seed.This finding is in agreement with Aziz et al., (2014) where they found that pH did not have significant influence on the adsorption of ammoniacal nitrogen in a media. However, this work is on desorption of NO3 rather than adsorption. Also, significant variation of pH in the aquifer is not envisaged and is detrimental to the denitrifying bacterias.

It has been previously established that organic matters are used as electron donors in denitrification (Shin et al., 1999). In this research attention is given to relevant parameters before coinsideration of any organic substrate in denitrification prcesess. These parameters include, oxygen bearing radicals , chloride , organic acids and water absorbance capacity of the substrate. Fig. 4. Shows the distribution of the parameters and from the figure, dates seed is observed to have the lowest values of all the parameters (except for chlorides), and hence considered as the most suitable.

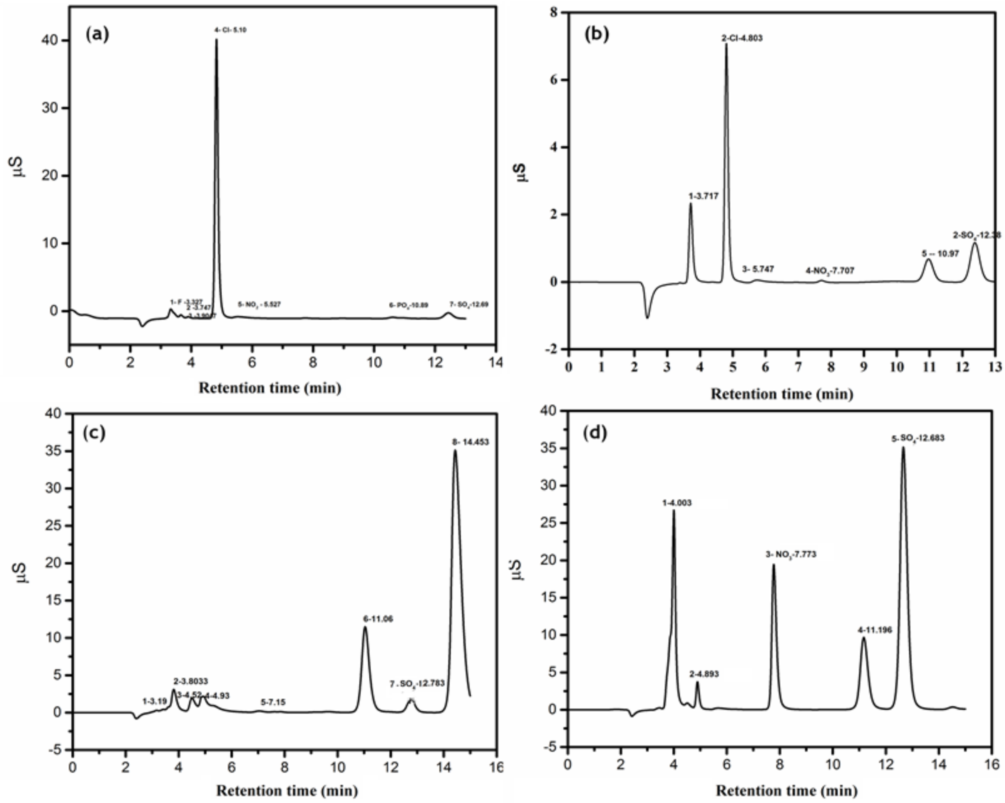

Fig. 2 Ion chromatography spectra of (a) Date seed (b) Moringa seed (c) Tamarind seed (d) Adsorption of NO_3^- on Tamarind.

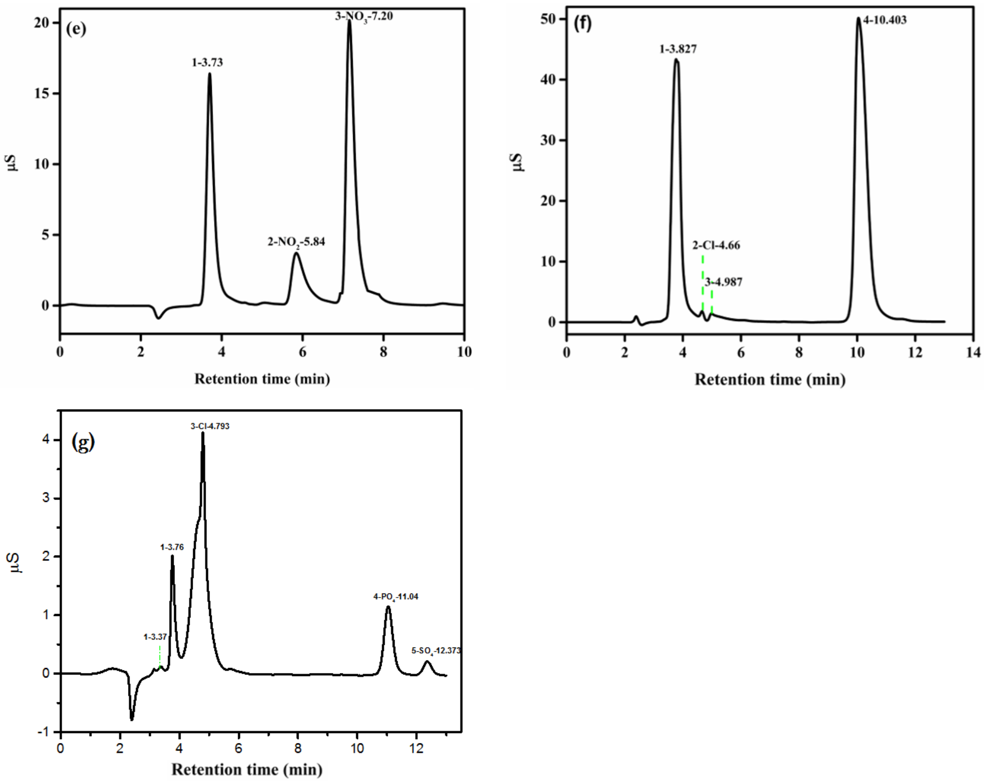

Fig. 3 Ion chromatography spectra of seed (e) Absorption of NO_3^- by Date seed extract (f) HCl treated Date seed Extract (g) KOH treated Date extract.

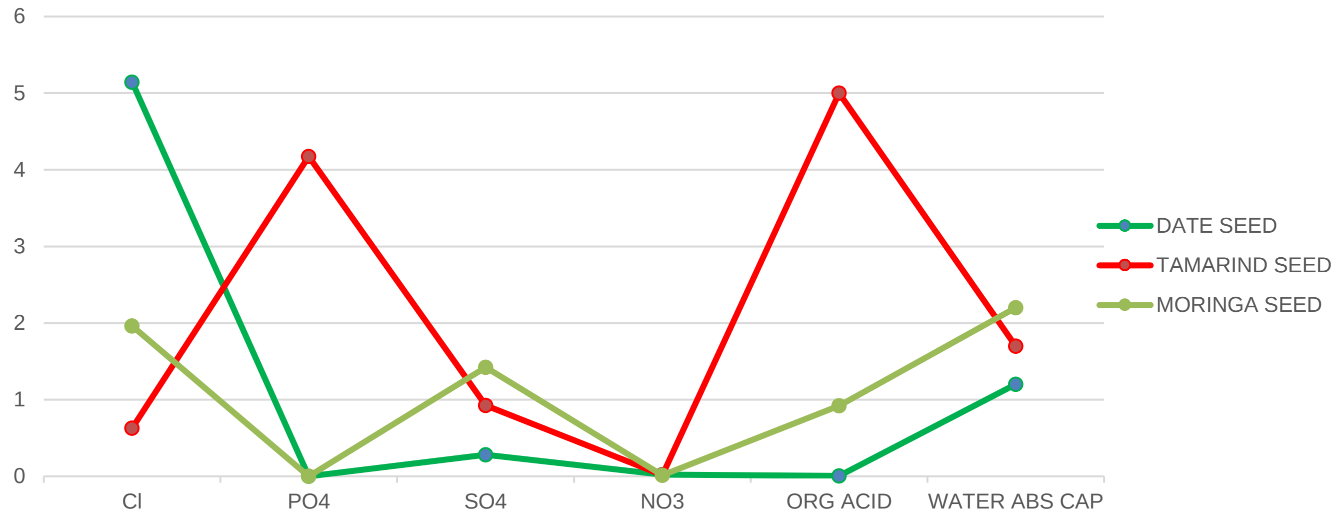

Fig. 4 Distribution of the selection parameters in the organic substrate.

CONCLUSION

The extraction methods employed for aqueous extraction of anions and related component at ambient temperature revealed that ultrasonic assisted extraction is more effective than the agitation assisted extraction. Variation of pH in the medium revealed that lower pH shifts the retention time backward and generates peaks within the region of phosphates. On the other hand, higher pH exposes the water deep and suppots the release of chloride from the seed. However, it is observed that neither basic nor acidic medium enhances NO_3 adsorption/extraction capacity of the seed.

Based on the results obtained using IC, caution should be taken before using tamarind seed as a carbon source in any denitrification process.This is because of intense pigmentation, high sulphate and phosphate ions concentration respectively. Additionally, untagged peaks were observed at organic acid region .

Moringa Oleifera seed was observed to contain moderate amount of sulphate. Despite the competative role of sulphate with nitrate, the moringa seed is recommended to be utilized in small amount. This is because, SO_4 has been linked to contribution in autotrophic denitrification.

The date seed was however found to be suitable for the purpose as it possess the quality of high percentage of carbohydrate , slow degradation process and less objectionable components. It is recommended that further research be conducted to determine composition of the date seed's degradation by- products to avert pollution swapping. (Shin et al., 1999)

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