Sorption of trichloroethylene and perchloroethylene onto a perlite/peat mixture.

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Abstract. Expanded perlite and peat are effective sorbents of organic pollutants; and their mixture would have improved mixing properties, increased organic matter content; and better price compared to individual materials. Therefore sorption of trichloroethylene and perchloroethylene to a 1:1 mixture of both materials was studied. Freundlich isotherm fitted best the data for trichloroethylene, with sorption coefficient of 15.9 ± 1.1 $(cm^3/g)^{(1/0.711)}$ and the Freundlich exponent of 0.711. The sorbed concentration ranged from 1.4 to 80 $\mu g/g.d.w$ and the dissolved values varied between 0.1 and 9.8 $\mu g/cm^3$. Sorption of perchloroethylene followed the linear isotherm with the sorption partition coefficient of 20.6 ± 0.3 cm^3/g. The dissolved equilibrium concentration values ranged from 0.1 to 8.7 $\mu g/cm^3$, while concentrations in the solid phase ranged from 2 to 180 $\mu g/g.d.w$. Percentages of removal were between 19 and 47 % for trichloroethylene; and between 23 and 30 % for perchloroethylene. Shape of the trichloroethylene isotherm indicated that rate of desorption was higher than the rate of sorption, while compound partitioning into the sorbent matrix governed the shape for perchloroethylene. Results obtained suggest the 1:1 mixture of expanded perlite and peat is an effective soil additive in remediation operations.

Keywords: trichloroethylene, perchloroethylene, perlite, peat, remediation

1. Introduction

Perlite is a volcanic glass which is rich in silica [1]. It has been used since the 1960's in the form of crushed rock (crude perlite) and as the expanded perlite which is obtained by heating of the crude perlite to around 871 ºC [1]. Crude perlite is an additive in potting soils [2]. Expanded perlite is mainly used in the construction industry to prepare concrete aggregates and formed products; and it is also an additive in the masonry-fill and cavity-fill insulations [2]. However, scientific reports have surfaced recently that show the ability of expanded perlite to stimulate removal of phenoxyacetic acid in constructed wetlands by sorption [3]. Bulk perlite has been successfully tested as a sorbent for copper, diuron, 3,4-dichloroaniline and glyphosate from model liquid matrices [4]. This indicates the potential application of perlite materials as sorbents in remediation operations of contaminated environments. Peat is an organic soil containing high concentrations of soil organic matter [5] and it has been shown to sorb trichloroethylene (TCE) and perchloroethylene (PCE; [6]). These are used as degreasing solvents in a wide range of industries [7] and solvents in dry-cleaning operations [8]. Environmental contamination with these solvents occurs through leakage from underground storage tanks and from accidental spills [9]. Prices of expanded perlite ranged from 279 to 302 USD between 2008 and 2009 [2], while the price of peat generally varies between 130 and 200 USD per metric ton [10]. A mixture of perlite and peat would have the following advantages as a sorption medium in remediation operations over the individual materials: addition of perlite would improve the mixing properties of the peat, while the addition of peat is likely to improve the sorption potential of perlite towards organic compounds by increasing its organic matter content. Mixture of the two materials would be a more cost-effective option over the pure counterparts. Therefore this study was aimed at investigating its sorption characteristics for TCE and PCE on a 1:1 mixture of both materials.

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2. Materials and Methods

2.1. Chemicals and consumables

Sigma-Aldrich (Johannesburg, South Africa) was the purchase source for TCE, PCE, methanol, ethyl acetate, glass beads, 10 cm³ glass pipettes, 2 cm³ clear glass GC vials with screw caps and the PTFE-lined silicone septa, 10 mm³ Hamilton syringe, 10 cm³ Fortuna optima glass syringe, 20 cm³ GC headspace vials (total volume calibrated at 22.0 cm³) and 50 cm³ volumetric flasks. Water for all experiments was produced using the MilliQ water purification system (MilliQ water; Microsep, Port Elizabeth/Johannesburg, South Africa). The stainless steel magnetic crimp top caps with the PTFE-lined silicone septa (referred to as crimp caps in further text) were purchased from Anatech Technologies (Sloane Park, South Africa). All GC/FID analyses were performed gases with purity of 99.999% or higher (Afrox-Linde Gas, Port Elizabeth, South Africa). Expanded perlite was purchased from InFiGro (Johannesburg, South Africa), while peat was purchased from D&A Timbers (Grahamstown, South Africa). The sorbent for experiments was prepared a 1:1 mixture (w/w) of the two materials by dry mixing on the day of the experiments.

2.2. Sorption methodology and principles of data evaluation

Sorption isotherms were measured using a combination of the headspace GC analysis and batch equilibration technique. First, 1.00 g of the perlite/peat mixture was weighed using the Pioneer PA2102 balance (Ohaus Corporation, Pinebrook, New Jersey, USA) out into a 20 cm³ GC headspace vial; and MilliQ water was added to adjust the total volume of the suspension in the GC vial to 15 cm³. A second vial is prepared in the same manner but with glass beads instead of the perlite/peat mixture (mass balance control). Stock solutions of TCE and PCE were prepared by weighing out neat compounds (accuracy 0.0001 g) on the Pioneer PA214 analytical balance (Ohaus Corporation, Pinebrook, New Jersey, USA) and complete dissolution in methanol inside a 50 cm³ volumetric flask. Different volumes of the stock solutions were then used to spike to vials with the perlite/peat mixture and the glass beads to achieve initial aqueous phase concentrations from 0 to 20 mg/dm³. Vials are immediately sealed with crimp caps and placed on the Orbital Shaker SS70 (Chiltern Scientific/International, Berkshire, United Kingdom); and incubated at 140 rpm in the dark at 30 °C for 48 hour. The incubation period was sufficient to achieve sorption equilibrium based on published literature data for chlorinated solvents [4]. Incubation temperature was chosen to represent ambient conditions in South Africa.

For the above-mentioned experimental set-up, the total amount of TCE or PCE present in each of the spiked vials is constant and referred to as m_T in further text. At equilibrium, the mass balance for the studied compounds in each of the GC vials can be expressed using Eq. (1).

$$m_T = C_{g1} \times V_{g1} + C_{L1} \times V_{L1}$$
$$m_T = C_{g2} \times V_{g2} + C_{L2} \times V_{L2} + X$$

(1)

The first of the two expressions in Eq. (1) refers to the control vial while the second one describes the mass balance for the perlite/peat mixture vial. In Eq. (1), $C_{g,L}$ stand for the gas phase (subscript g) and aqueous phase (subscript L) concentrations of TCE or PCE (units of μg/cm³), $V_{g,L}$ stand for the volume of the gas phase (subscript g) and aqueous phase (subscript L; both in units of cm³). Lastly, X stands for amount of TCE or PCE sorbed to the perlite/peat mixture (μg). Subscript 1 refers to the control vial the glass beads and subscript 2 stands for the vial with the perlite/peat mixture. The following properties of the system are constant: m_T, V_g and V_L. Using the Henry's law, dimensionless Henry's law constant and X can be expressed using Eq. (2).

$$H = \frac{C_g}{C_L}$$

$$X = (C_{g1} - C_{g2}) \times \left[V_g + \frac{V_L}{H} \right]$$

(2)

Definition of the solid phase concentration S (μg/g dry weight; in further text as μg/g.d.w.) is in Eq. (3).

$$S = \frac{X}{D} \tag{3}$$

In. Eq. (3), D is the dry weight of the solid support medium present in the system (perlite/peat mixture; grams dry weight; in further text as g.d.w.), as determined by drying to constant weight at 105 ºC using the UFE 700 oven (Memmert, Schwabach, Germany) and equal to 69.2 %. C_L was of TCE and PCE in the aqueous phase of the system were calculated using Eqs. (1)-(3) and quantified as described below.

2.3. GC analyses of the sorption isotherm samples

After the 48 hours incubation period, all vials were placed in autosampler of the CombiPal system (CTC Analytics/Anatech Technologies, Sloane Park, South Africa), incubated at 500 rpm and 30°C for 2 minutes. Then stirring was discontinued and the vial headspace was sampled using the CombiPal autosampler (150 mm^3); the C_g values for TCE and PCE were determined by injecting the headspace samples into the 3800 Varian GC equipped with a flame ionization detector (SMM Instruments, Johannesburg, South Africa); and a DB-VRX capillary column (30 m × 0.25 mm × 1.4 µm; Agilent Technologies, Johannesburg, South Africa). The column temperature programme started at 50 °C for 3 minutes, ramp to 85 °C at 10 °C/min, then ramp to 200 °C at 20 °C/min and hold for 1.75 minutes. Injector temperature was set to 180 °C and the detector temperature to 200 °C; and peak heights were used for quantitative analyses as described below.

2.4. Determination of Henry's law constants for TCE and PCE

Before sorption equilibria can be characterized using Eqs. (1)-(3), the dimensionless Henry's law constants (H) for TCE and PCE. This parameter has been shown to vary with the equilibrium concentration of the tested compounds in the aqueous phase [11]. Values of H were determined using the modified methodology of Cheng et al. [12], with liquid injections used for the GC calibrations to improve reproducibility; and H was calculated using Eq. (4) and (5).

$$C_g = \frac{P}{k \times V_{Sample}} \tag{4}$$

$$H = \frac{V_L \times C_g}{m_T - V_g \times C_g} \tag{5}$$

In Eq. (4), P stands for the peak height (mV) from the GC/FID and V_{Sample} is the volume of the headspace taken at equilibrium (150 mm^3); k is the slope of the calibration curve for TCE and PCE based on liquid injections (mV×cm^3/µg). Stock solutions for the liquid injections were prepared in methanol for TCE and in ethyl acetate for PCE. Analyses were performed as described for the sorption isotherm measurements. Terms in Eq. (5) have the same meaning as described in Eqs. (1)-(3).

3. Results and Discussion

The dimensionless Henry's law constants varied from 0.860 to 1.152 for TCE; and from 0.348 to 0.456 for PCE. Sorption of TCE onto the perlite/peat mixture followed the Freundlich sorption isotherm in Eq. (6), while the PCE data followed the linear sorption isotherm in Eq. (7).

$$S = K_f \times C_L^N = 15.9(\pm 1.1) \times C_L^{0.711 \pm 0.030}; R^2 = 0.997 \tag{6}$$

$$S = K_D \times C_L = 20.6(\pm 0.3) \times C_L; R^2 = 0.999 \tag{7}$$

In Eq. (6), K_f is the Freundlich sorption coefficient ($^{0.711}\sqrt{cm^3/g}$), and N is the Freundlich exponent (dimensionless). In Eq. (7), K_D is the sorption partition coefficient (cm^3/g). The S values for TCE ranged from 1.4 to 80 µg/g.d.w, while the C_L interval varied between 0.1 to 9.8 µg/cm^3. For PCE, the C_L values were inside the following interval: 0.1-8.7 µg/cm^3, while the sorbed phase concentrations ranged from 2 to 180 µg/g.d.w. The percentage of m_T which sorbed to the perlite/peat matrix at equilibrium was calculated using Eq. (8).

$$Percent\,sorbed = 100 * \frac{m_\text{T} - m_\text{Final}}{m_\text{T}}; \%$$

(8)

Values for this parameter ranged 19 to 47 % for TCE and from 23 to 30 % for PCE. Huguenot et al. [4] measured the percentage sorbed for 3,4-dichloroaniline ranged from 44-64 %. For phenoxyacetic acids' sorption onto perlite, the S values were reported lie between 5 and 30 µg/g.d.w. [3]. Sorption of perchloroethylene to peat moss has been shown to follow Freundlich isotherm and the organic carbon content had been shown to be the most important factor governing the extent of sorption [13]. Thus percentages sorbed in this study are comparable or slightly lower than the literature values, while the S intervals of TCE and PCE span a wider interval than reported in the literature. The linear sorption isotherm observed for PCE indicates that the main sorption mechanism for this compound was partitioning into the sorbent matrix [14]. As the sorption to peat materials has been shown to follow the Freundlich isotherm, the addition of perlite changes the sorption mechanism for PCE in contrast to pure peat.

Sorption of TCE to SRS Wetland peat has been shown to follow Freundlich sorption isotherm with the K_f values of 59.188 ($^{0.7446}\sqrt{cm^3/g}$) and the N value of 0.7446 [15]. The K_f values in this study is lower than the value observed in the SRS Wetland peat, while the Freundlich exponent value is comparable to the study of Ozturk et al. [15]. The most probable reason for the difference in K_fs is that the experiments in this study were performed at 30 °C, while Ozturk et al. [15] performed theirs at 20 °C. At equal N value, the lower the temperature of incubation, the stronger the sorption and the higher the K_f value. Freundlich isotherm was also observed for TCE sorption to peat moss [16]. Therefore the peat was probably the dominant site of TCE sorption to the perlite/peat mixture. At the same time,, the sorption capacities seem to be comparable between the perlite/peat mixture and the peat, i.e. they can substitute each other as amendments in remediation operations. Skopp [17] derived the Freundlich sorption isotherm by applying fractal kinetics to describe rates of sorption and desorption to obtain Eq. (9).

$$S = K_\text{f} \times C_\text{L}^\text{N} = \left(\frac{L_1}{L_2}\right)^{\frac{1}{N_2}} \times C_\text{L}^{\frac{N_1}{N_2}}$$

(9)

In Eq. (9), L_1 is the fractal rate constant of sorption in Freundlich isotherm ($^N\sqrt{h^{-1}}$) and L_2 is the fractal rate constant of desorption in Freundlich isotherm ($^N\sqrt{h^{-1}}$). Based on the Eq. (9), it can be concluded that N is equal to the ratio of N_1 and N_2. If N_1 is lower than N_2, then the sorption is kinetically of a lower order than desorption, i.e. the N value is lower than 1.00. This is the case for sorption of TCE onto the perlite/peat mixture where $N = 0.711$.

4. Conclusions

Results of this study indicate that the sorption of TCE and PCE onto the perlite/peat mixture follows different mechanisms. Percentage of sorption proved that this mixture can be a viable sorbent for the removal of TCE and PCE from contaminated environments, e.g. soil amendments during remediation operations, as the respective values ranged from 19 to 47 % for the two compounds depending on the C_L values.

5. Acknowledgements

6. References

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