Soil Adsorption Capacity: Theory vs. Experiment

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Summary: The adsorption capacity of phenol on a granite residual soil and a commercial kaolinite were evaluated. Langmuir's theory and adsorption parameters from low concentration batch tests were used for prediction of this capacity. These were then compared with tests at high concentrations. Low concentration results were highly linear and thus the adsorption constants can be easily obtained. Tests at high concentrations were non-linear especially when adsorption is at its maximum, thus permitting experimental determination of maximum adsorption capacity. From this study, it is concluded that maximum adsorption capacity can be reliably obtained using Langmuirs's theory using results of low concentration tests. It is also envisaged that the granite residual soil has a great potential for use as a soil liner material due to its excellent adsorption property.

INTRODUCTION

Adsorption involves the preferential partitioning of substances from the gaseous or liquid phase onto the surface of a solid substrate. In general industrial applications, from the early days of using bone char for decolourisation of sugar solutions and other foods, to the later implementation of activated carbon for removing nerve gases from the battlefield, to today's thousands of applications, the adsorption phenomenon has become a useful tool for purification and separation. Adsorption phenomena are operative in most natural physical, biological, and chemical systems, and adsorption operations employing solids such as activated carbon and synthetic resins are used widely in industries and for purification of waters and wastewaters. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate. Adsorption is thus different from absorption, a process in which material transferred from one phase to another (e.g. liquid) interpenetrates the second phase to form a "solution". The term sorption is a general expression encompassing both processes. With respect to geo-environmental applications, adsorption is important to assess the migrational characteristics of the solute in the particular soil in question. The more it is adsorbed, the lesser its migration and less extensive will be the extent of pollution.

Residual soils are mainly found in tropical climates as a result of heavy rain and consistently high temperatures. For example, 75% of the Malaysian Peninsular is covered by residual soils (Taha and Debnath 1999). Studies on such soils have not been extensively conducted and thus the majority of technical and scientific information have been derived mainly from studies on soils of different origin i.e clays. This provides problems in many practical situations as the results cannot be readily extrapolated from soil to soil. Taha (2000) demonstrated that the differences in the formation of residual and sedimentary (such clay) soils would likely to result in soils of different characteristics.

The study conducted in this paper is aimed towards understanding the adsorption interaction between phenol and a residual soil, i.e. decomposed granite or granite residual soil, in batch adsorption tests. Phenol is an organic compound widely used in industries such as in the manufacturing plastics, lubricants, paints, pharmaceuticals, herbicides, and resins. Chemically, phenol is a hazardous chemical and if absorbed through skin, inhaled, or swallowed may lead to serious injuries and/or fatalities. One of the major hazards of phenol is its ability to penetrate the skin rapidly. Therefore most phenolic compounds are priority pollutants. For example, the United States Environmental Protection Agency established the drinking water standard for phenol at 1 ppb or less (Acar et al. 1992). Batch tests to determine sorption parameters has been known and practiced for a long time. It can provide a quick overview of the sorption processes to be expected and the maximum mass of the contaminant to be adsorbed (Holzlohner et al. 1997). The Langmuir adsorption theory has been in the literature for almost a decade. However, it is being continuously used due to its versatility in analysing adsorption test results. It must be emphasised that the Langmuir's adsorption theory to predict the maximum adsorption capacity still rely on test results in order to obtain the required parameters. This will be discussed in the following section.

LANGMUIR ADSORPTION THEORY

The Langmuir adsorption theory or isotherm (Langmuir 1918) originally developed for adsorption of gasses on solids surfaces is based on the concept that surfaces have finite adsorption sites. When all the adsorption sites are filled, the surface will no longer be able to adsorb solute from solution. Therefore, this isotherm offer an advantage over the other adsorption isotherms (e.g. linear and Freundlich) in that it put a cap on the amount of chemical species the soil can adsorb. Thus, the maximum amount of solute adsorbed in a particular soil-chemical interaction system can be estimated. Analytically, the isotherm may be written as

$$q = \frac{\alpha \beta C_e}{1 + \alpha C_e} \tag{1}$$

where q is the amount adsorbed i.e. "capacity" parameter, α is the adsorption constant related to the binding energy or the "affinity" parameter, β is the maximum amount of solute that can be adsorbed by the soil, and C_e is the equilibrium concentration. These parameters can be easily obtained from its linearised form:

$$\frac{1}{q} = \frac{1}{\alpha \beta} \frac{1}{C_e} + \frac{1}{\beta} \tag{2}$$

A plot of $1/q$ vs. $1/C_e$ can be used to obtain the isotherm parameters.

MATERIALS AND PROCEDURES

Materials

Phenol (C_6H_9OH) is also commonly known as carbolic acid. The compound used in this study is a product of Mallinckrodt Baker, Inc., New Jersey, USA and is supplied as colourless to pink crystals.

The residual soil used in this study is obtained from a granite formation about 8 km just south of Kuala Lumpur, the capital city of Malaysia. The soil was dug out from about 20-45 cm below the surface. In the laboratory, it was air-dried for fifteen days, roots were separated from the bulk soil and stored in polythene bags until ready for use. Kaolinite was purchased from Kaolin (Malaysia) Inc. Some basic properties of the soil and its grain size distribution are shown in Table 1 and Figure 1, respectively.

Table 1. Basic Soil Properties

Property	Residual soil	Kaolinite
Specific Gravity, G_s	2.55	2.63
Nat. Moisture Content,(%)	31	
Liquid Limit, LL (%)	76.3	74.2
Plastic Limit, PL (%)	27.5	41.5
pH	4.60	5.16
Organic Content (%)	1.37	0.88
Cation Exchange Capacity CEC, (mmol charge/100g = meq/100g)	8.96	9.91
% clay	46	31

Testing Procedures

Phenol solutions were prepared using de-aired water. Batch adsorption tests (i.e. tests on individual samples) were conducted on soil suspensions where the soil particles were exposed and available for interaction with the phenol solution. Soil samples for batch equilibrium tests were air dried and sieved through a 63 μm sieve. Basically the procedure consists of shaking 12 grams of air-dried soils with a series of phenol solutions of different concentrations for 24 hours in a conical flask. The mixture was then allowed to equilibrate for 2 weeks before the final fluid concentrations were analysed using a Shimadzu UV-1601PC spectrophotometer. Detection wavelengths used were between 200 and 350 nm.

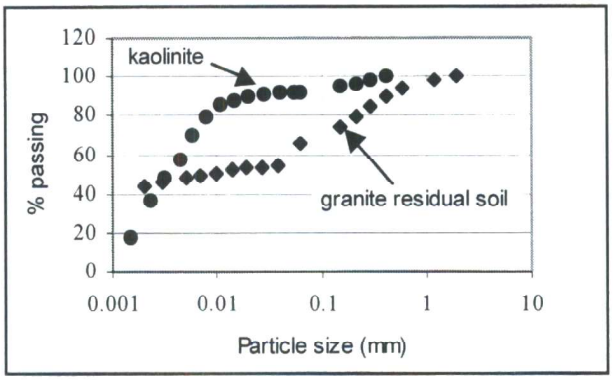

Figure 1 The grain size distribution of the soils

The amount of phenol adsorbed, q, was then calculated using the following equation

$$q=(C_o-C_e)\frac{V}{M} \qquad (3)$$

where C_o is the initial concentration, C_e is the final or equilibrium concentration, V is the volume of solution (fixed at 60 mL in this study), and M is the mass of soil used.

The pH of water used for the preparation of phenol solutions is an important parameter and must be thoroughly checked each time the solutions were prepared. This is to ensure results are not affected as variations of the pH of distilled water can be quite extreme due to many reasons such as poor maintenance of equipment. A range of pH value between 6.5 and 7.5 was established and distilled water that does not meet this standard was rejected during solution preparation.

RESULTS AND DISCUSSION

The initial pH of the phenol were between 5.52 and 6.05. At the end of the tests the range of pH of the solutions for the granite residual soil and kaolinite were between 3.92 to 4.16, and 5.30 to 5.95, respectively. This further establishes that the residual soil is more acidic than the commercial kaolinite. The pH results can be used to evaluate the buffering capacity of the soil. It is shown that the changes in the final equilibrium pH are slightly lower than the original pH with the phenol-kaolinite system showing better stability. Thus, the kaolinite has better buffering capacity than the residual soil.

Saltzman and Yariv (1975) demonstrated that phenol could act as a cation (H^+ acceptor) in acid solutions and an anion (H^+ donor) in basic environment. In this study, since both the soil and solutions are acidic, it is apparent that phenol will be positively charged and adsorbed primarily by the negatively charged surface of the soils.

At low concentrations (for initial concentrations C_o lower than 10 mg/L) the results can be approximated by a linear adsorption isotherm (Figures 2 and 3). The slope of the line in the figures is the partition coefficient K_d, which is one the most important parameters in modelling the advective-dispersive transport of contaminants in soil. The corresponding values for the interaction of phenol on the residual soil and kaolinite are approximately 10.48 L/kg (R^2=0.96) and 1.18 L/kg (R^2=0.93), respectively. This observation indicated that phenol has a greater affinity (about 1 order magnitude greater) to the residual soil compared to kaolinite. This is possibly due to the higher clay (fines) content of the residual soil which generated greater surface area available for adsorption to take place. The amount of organic is also greater in the residual soil which may have attracted the phenol molecules in greater amounts possibly through hydrophobic sorption processes usually found with neutral or organic compounds.

The linearised adsorption isotherm for Langmuir analysis is shown in Figure 4. The α and β values for the granite residual soil are 17.54 L/mg, and 238.10 mg/kg, and 6.33 L/mg, and 23 mg/kg, respectively for kaolinite. Both parameters indicated a more favourable adsorption of phenol onto the granite residual soil compare to that of the kaolinite. The β values for both soils again prove (as in the K_d values) that the granite residual soil is able to adsorbed a maximum of 10 times as much (1 order of magnitude) phenol.

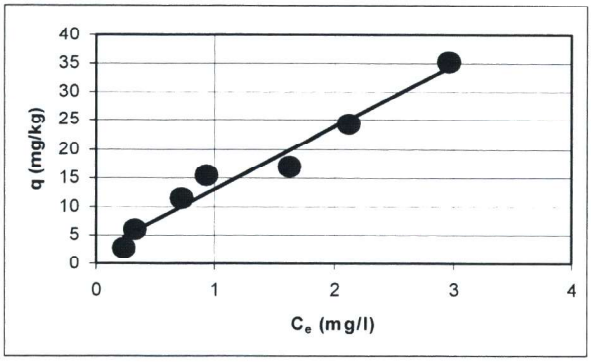

Figure 2. Linear adsorption isotherm for phenol-residual soil series at low concentrations.

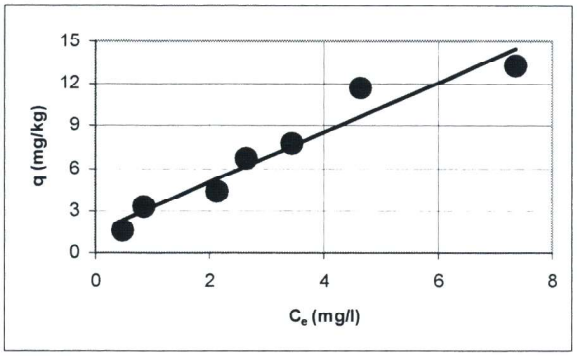

Figure 3. Linear adsorption isotherm for phenol-kaolinite series at low concentrations.

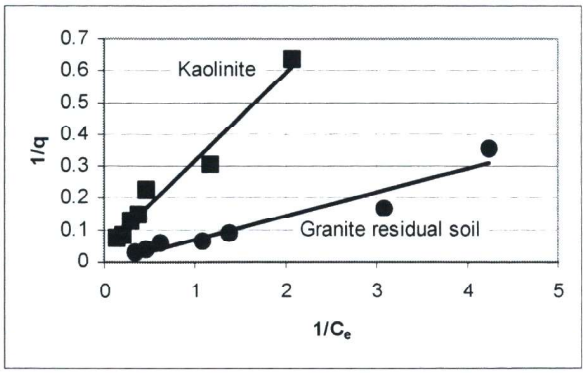

Figure 4. Linearised Langmuir adsorption isotherm for phenol-soil interaction.

The linearised adsorption isotherms for Langmuir analysis for all test data (Co ranging between 0 - 100 mg/L) are plotted in Figure 5. The figure illustrate that at low concentrations sorption increases linearly with equilibrium concentration until it levels off at certain "threshold" adsorption. At this point maximum adsorption is observed, possibly due to maximum capacity of the adsorption sites as mentioned in Langmuir's theory. The "threshold" adsorption is estimated approximately 245 mg/kg for the granite residual soil and 28 mg/kg for kaolinite. This compare quite favourably with the estimated value from the low concentration analysis which were 238.10 mg/kg, and 23 mg/kg, respectively, for the granite residual soil and kaolinite. Thus, the low concentration results may be used to estimate the adsorption capacity of phenols on the soils. In essence, the procedure omits the necessity of running tests at higher concentrations or the number of tests at higher concentrations can be greatly reduced for determination of maximum capacity of a particular soil to adsorb

chemical species. This practice reduces the amount of contaminated waste materials generated from testing procedures and also reduces exposure of operators to high concentration chemicals.

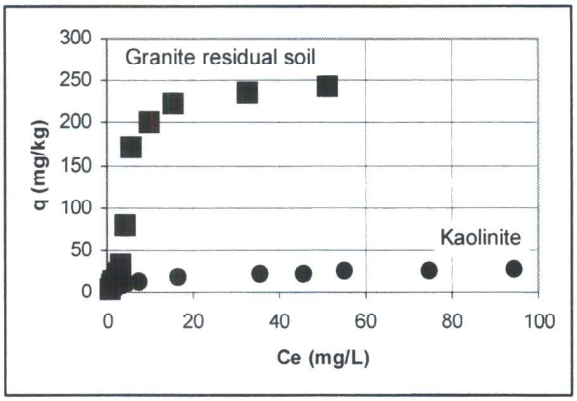

Figure 5. Results of soil-phenol adsorption interaction for all test results.

Figure 5 also provide another important observation, i.e. the tests results over the range of concentration conducted in this study significantly deviate from the linear relationship as obtained when only the low concentration results were analysed. Thus a unique slope of line (the partition or distribution coefficient, K_d) is only valid for cases at low concentration and it varies thereafter as the slope of the line changes with the equilibrium concentration. An important repercussion of this observation is that despite the results of this study and many others which indicated that K_d is not unique and highly non-linear, this important parameter is usually taken as unique in the advective-dispersive transport models for any levels of concentration. The use of linear relationship, especially drawn as the initial tangent, will result in high K_d meaning high adsorption, thus underestimating contaminant transport. As a result, the extent of contamination is also underestimated. Attempts have been made to include non-linear isotherms in the transport equation however the formulations are still not well established and will unlikely yield satisfactory estimates (Shackelford 1993).

It has been shown that the granite residual soil adsorbed greater amounts of phenol compare to that of kaolinite. Taha and Debnath (1999) obtained similar results for the study of adsorption of cyanide. From these studies, it can be concluded that the granite residual soil is a better adsorptive material. In addition, it was found that the permeability of the soil is in the order of 10^{-7} cm/s (Mofiz 2000). Thus, it has great potential to be used as a soil liner material for the construction of landfills. At the moment clay liner using kaolinite as the main mineral is recommended in many standards. This recommendation is a result of extensive research work and data available on such material. In tropical and developing countries, where residual soils are plentiful, the use of this local material can lead to extensive construction cost reduction. Simultaneously, this would stimulate enhancement in waste management program through the construction of more engineered landfill. However, more studies will be required in order to obtained a more efficient field application of granite (and other) residual soil.

CONCLUSIONS

The maximum adsorption capacity of phenol on granite residual soil and kaolinite were studied from batch adsorption tests. Experiments were conducted at initial phenol concentrations ranging between 0.8 to 100 mg/L. Analyses were made using the linear, and Langmuir adsorption isotherms. Result from low concentration predictions using Langmuir's theory compare quite favourably compared to that from testing results obtained at higher concentrations. Thus, experiments at higher concentrations are not necessary or reduced to minimum. This will reduce experiments contaminated wastes and exposure of personnel to high concentration hazardous chemicals. It was also found that the residual soil possesses greater adsorption capacity compare to that of kaolinite. The granite residual soil could adsorb as much as 10 times more phenol compared to that of kaolinite. However, kaolinite has a better buffering capacity. The results also showed that adsorption data obtained over the range of phenol concentrations conducted in this study did not produce a singular or linear partition coefficient, K_d. From this study, it is also concluded that the granite residual soil has a great potential for use as a soil liner material.

REFERENCES

Acar, Y.B., Li, H., and Gale, R.G. (1992). Phenol removal from kaolinite by Electrokinetics, *J. Geotechnical Engineering*, ASCE, Vol 118, No. 11, Nov., pp. 1837-1852.

Holzlohner, U., August, H., and Meggyes, T. (1997.) Contaminant transport, fundamentals and minimisation, in *Advanced Landfill Liner*, August, H., Holzlohner, U., and Meggyes, T. eds, Thomas Telford, London, pp. 31-37.

Langmuir, I. (1918). The adsorption of gasses on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40: 1361-1382.

Mofiz, S.A. (2000). Behaviour of unreinforced and reinforced residual granite soil, *PhD thesis*, Universiti Kebangsaan Malaysia, 315 p.

Saltzman, S., and Yariv, S. (1975). Infrared study on sorption of phenol and p-nitrophenol by montmorillonit, *Soil Sci. Soc. Am. Proc.*, 39(3), pp. 474-479.

Schackelford, C.D. (1993). Contaminant transport, in *Geotechnical Practice for Waste Disposal*, Daniel, D.E. eds, Chapman and Hall, London, pp. 33-63.

Taha, M.R. (2001). Some aspects related to clean up of contaminated soils, *Proc. Brownfield 2001*, Institution of Engineers Malaysia.

Taha, M.R., and Debnath, D.K. (1999). Interaction of cyanide with residual soil and kaolinite in batch adsorption tests, *Journal Institution of Engineers Malaysia*, Vol. 60, No. 3, September, pp. 49-57.

Veith, J.A., and Sposito, G. (1977). On the use of the Langmuir equation in the interpretation of adsorption phenomena, *J. Am. Soil Sci. Soc.*, 41:697-702.