



The measurement of the specific surface area of soils by gas and polar liquid adsorption methods—Limitations and potentials

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ABSTRACT

The specific surface area (SSA) of soils is a basic property and closely related to other physical and chemical properties like e.g. cation exchange capacity, clay content, organic matter content, porosity and hydrodynamic and geotechnical characteristics. Therefore, the SSA of soils has been measured frequently for decades. However, no universal method to determine SSA exists. The existing methods can generally be grouped into two categories, the adsorption of gases and the adsorption of polar liquids or molecules from solution. Depending on the method applied, the SSA of a soil can vary, as by these different methods, different surfaces of the soil are determined. The most frequently used representatives of these two groups for measuring SSA of soils are the physisorption of nitrogen gas at 77 K (BET-N₂) for the gas adsorption methods, yielding the external surface area of the mineral particles, and the retention of ethylene glycol monoethyl ether (EGME) for the adsorption of polar liquids, probing the total surface area including interlayers of clay minerals and micropores of organic material. Studies dealing with the determination of SSA of soils are numerous, and it has also been shown that the resulting SSA values differ not only depending on the method but also on the sorbate used and the sample pretreatment. This review shortly presents the principles of these methods and emphasises their limitations and difficulties, when applied to soil samples, like sample pretreatment, (micro-)porosity and attachment of organic material to mineral surfaces. In particular the drying of the samples prior to measurement seems to be crucial for the results obtained. Recommendations are given in order to improve the quality of the data and to facilitate the comparability of SSA data of different studies. It is shown for clayey soil samples that the relationship between BET-N₂ and EGME SSA depends predominantly on the type of clay mineral and not on the content of organic material. Thus, from the SSA measurements, an estimation of the dominant clay mineral seems possible. Consequently, a suitable combination of various SSA determination methods together with related techniques can result in a more detailed characterisation of the reactive interface of a soil to the liquid and gaseous phases.

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1. Introduction

Soils consist of a mixture of various organic and inorganic components interacting with each other and thereby forming a heterogeneous interface between the solid and the liquid and gaseous phases of the soil (Totsche et al., 2010; Young and Crawford, 2004). The characterisation of the solid surface is essential to understand the fate and effects of dissolved and dispersed substances entering the soil because the surface provides a multitude of various reactive sites (Totsche et al., 2010). The size of this surface is a fundamental parameter, as a larger surface area can provide more reactive sites and thus more possibilities of a substance to interact with the solid soil constituents during its travel through the soil. The surface area between the solid and the liquid and gaseous phases of a soil is a property of the solid, which is called specific surface area (Chiou et al., 1993). The specific surface area (SSA) is defined as the mass normalised surface area (e.g. Metz et al., 2005) and is a basic soil property. Many physical and chemical soil properties are influenced by or closely related to the SSA like e.g. cation exchange capacity, clay content, organic matter content, porosity and hydrodynamic and geotechnical characteristics (Feller et al., 1992; Petersen et al., 1996; Theng et al., 1999; Yukselen-Aksoy and Kaya, 2010b). Consequently, the SSA of soils has very often been determined during the last decades.

Although it seems that the determination of the SSA of soils is nowadays a more or less routine measurement, still no universal standard method exists. Rather, several methods have been proposed and are used to determine SSA. Generally, these methods can be divided in two groups, the adsorption of gases, i.e. the condensation of molecules on the solid surface, and adsorption of polar liquids including water or adsorption of molecules from solution onto the surface (Chiou et al., 1993; Gregg and Sing, 1967; Santamarina et al., 2002; Tiller and Smith, 1990; Yukselen-Aksoy and Kaya, 2010a). Depending on the type of method applied, the SSA of a soil can vary. Thereby, gas adsorption methods commonly yield lower values of SSA than the adsorption of liquids or molecules from liquids. It is widely accepted that gas adsorption measurements reveal only the external surface area, i.e. the entire surface surrounding the separate soil grains. On the other hand, methods involving liquids determine the total surface area, which includes additionally to the external surface area also the internal surface area, consisting of the surfaces of the interlayers of clays or micropores of organic material that are inaccessible to the gas molecules (Chiou et al., 1993; de Jong, 1999; Santamarina et al., 2002; Tiller and Smith, 1990; Yukselen-Aksoy and Kaya, 2010a). Besides, SSA can also be inferred from known thermodynamic properties, the dissolution rate of soluble minerals, microscopy, diffusiveness of X-ray diffraction patterns (Santamarina et al., 2002) and from atomic force microscopy measurements (Bickmore et al., 2002; Macht et al., 2011; Metz et al., 2005). But for soils, most commonly gas adsorption and adsorption of polar liquids are applied to measure SSA.

Studies dealing with SSA determinations of soils and also sediments are numerous. Subsequently, the objective of this review can therefore not be to give a complete overview of the entire literature available. Instead, it is intended to focus on the application of physisorption of nitrogen gas at 77 K as a representative of gas adsorption measurements and the retention of ethylene glycol monoethyl ether (EGME) as a representative of polar liquid adsorption measurements to soil samples. After a short introduction of the principles of the methods, special emphasis will be put on their inherent limitations and difficulties

for soil samples like sample pretreatment, (micro-)porosity and the attachment of organic material to mineral surfaces. Considering these aspects, a suitable combination of several diverse techniques can result in a more detailed characterisation of the soil's complex interface to its liquid and gaseous phases.

2. Gas adsorption

2.1. Physisorption of N₂ at 77 K according to the BET method

The physisorption of gas molecules is based on the attraction of molecules to a surface by dispersion forces, short-range repulsion forces and forces due to permanent dipoles within the adsorbed molecule. Contrary to chemisorption, no transfer of electrons between the adsorbed molecule and the solid takes place (Gregg and Sing, 1967; Sing et al., 1985). Thus, physisorption is able to probe all surface sites accessible to the gas molecules and not only those sites which possess some particular property, e.g. "acid" sites (Gregg and Sing, 1967). Suitable gases for physisorption include N₂, benzene, toluene, nitrous oxide, water vapour and inert gases like argon, krypton and xenon (Feller et al., 1992; Gregg and Sing, 1967). It is assumed that one gas molecule occupies a defined area of the surface. If the amount of gas that is necessary to cover the complete sample surface in a monomolecular layer, the so-called monolayer, is known, the SSA of the sample can be calculated from this monolayer capacity (Sing et al., 1985).

If the quantity of an adsorbing gas on a surface is measured over a wide range of relative pressures at a constant temperature, an adsorption isotherm is obtained. Similarly, desorption isotherms can be derived by measuring the quantities of gas removed from the surface, when the relative pressure is lowered. According to Brunauer et al. (1940), adsorption isotherms can be grouped into five types (Fig. 1). Type I is the so-called Langmuir isotherm and is a typical physisorption isotherm of microporous solids with relatively small external surfaces. According to the classification of the International Union of Pure and Applied Chemistry (IUPAC), micropores are defined as pores with a width not exceeding 20 Å, while pores with diameters of more than 500 Å are classified as macropores; pores of intermediate size are termed mesopores (e.g. Sing et al., 1985). For type I isotherms, the limited uptake is governed by the accessible volume of the micropores that determines the shape of the isotherm. Type II isotherms are sigmoidal isotherms, which are normally obtained with a nonporous or macroporous solid. They represent unrestricted monolayer-multilayer adsorption and often display a rather long straight portion. The point of inflection, where this linear portion begins, is termed point B and indicates the completion of the monolayer. Accordingly, point B represents the monolayer capacity. At higher relative pressure, the multilayer develops. Type IV isotherms are in the low pressure range comparable to type II isotherms. They exhibit a steep slope at higher pressures and hysteresis due to capillary condensation in mesopores (pore diameter of 20 – 500 Å). Whereas type IV isotherms are typical for many mesoporous industrial adsorbents, type III and type V isotherms are rarely encountered. Their convex shape is caused by stronger adsorbate-adsorbate interactions than adsorbate-adsorbent interactions. Such strong adsorbate-adsorbate interactions play only a role in a few systems, like e.g. nitrogen adsorption on polyethylene. Additionally, type V isotherms show hysteresis due to mesoporosity of the sample. Like for type III isotherms, the adsorbent-adsorbate interaction is weak, which is only obtained with certain porous adsorbents (Gregg and

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