

Specific Surface Area by Colorimetry and Image Analysis

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Abstract:	Specific surface area is more informative than grain size for fine-grained sediments where $S_s > 1m^2/g$. In fact, specific surface area plays a central role in engineering properties and processes in fine-grained soils including pore size and bioactivity; fabric, plasticity and rheology; hydraulic and electrical conductivity; compressibility and residual friction angle; and all forms of coupled processes. This research advanced a dye adsorption method using digital image colorimetry implemented with smartphone technology. In particular, adopted a water-based approach to reach internal surfaces in platy phyllosilicates, selected short dye molecules to reduce the range of potential molecular contact area, and developed a physics-based adsorption model to analyze the complete dataset to minimize the uncertainty in specific surface area determinations. The study involved fine-grained soils with distinct mineralogy and specific surface area (from 1 to 600 m ² /g), and various cationic dyes and a protein to explore the effect of molecular size and shape and pH effects. Crystal violet emerged as a reliable dye for soil characterization. Time-dependent measurements confirmed second-order kinetics and highlight the importance of adsorption time.

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1 2 3 4 5	27	List of notation	
6	28	A []	light absorbance
/ 8	29	$A_{ m v}$	Avogadro's number 6.02x10 ²³ [molecules/mol]
9 10	30	В	blue intensity
11 12	31	<i>c</i> [mg/L]	dye concentration in solution. Subscripts: 0: initial, d: dye, f: equilibrium, l: in the liquid
13	32	C_{α} [mol/g]	value of liquid concentration c_l when surface coverage $s_c = M_{sc}/2$
14 15	33	d100 [Å]	basal spacing
16 17	34	$d_{pore}[\mu m]$	mean pore size
18 19	35	e []	void ratio
20	36	G	green intensity
21 22	37	Н	hue (HSV)
23 24 25 26 27 28 29 30	38	Ι	transmitted intensity; I_0 incident light intensity
	39 40	k	rate constant of adsorption. Subscripts 1: first-order, 2: second-order, F: Freundlich isotherm and L: Langmuir isotherm
	41	<i>m</i> [g]	mass. Subscripts d: dye solution, dye: dye, s: soil, w: water
	42	M_d [g/mol]	molar mass of the dye
31 32	43	M_{sc} [mol/m ²]	maximum possible surface coverage as $c_l \rightarrow \infty$
33 34	44	n []	exponent Freundlich isotherm
35 36	45 46	<i>q</i> [mg/g]	adsorption capacity. Amount of solute adsorbed per mass of sorbent. Subscripts e: equilibrium, t: at any time
37 38	47	R	red intensity
39 40	48	S	color saturation (HSV)
41 42	49	$s_c [\text{mol/m}^2]$	surface coverage
43	50	S_{dye} [m ² /molec.]	contact area of the dye molecule with the mineral surface
44 45	51	$S_s \left[\mathrm{m}^2 / \mathrm{g} \right]$	specific surface area
46 47	52	<i>t</i> [min]	time
48 40	53	<i>V</i> [L]	volume of aqueous solution
49 50	54	V	value (HSV)
51 52	55	w [%]	gravimetric water content
53 54	56	ρ[]	form factor
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58 1. Introduction

The specific surface area relates the surface area to the grain mass and reflects the balance between surface-related particle level forces (such as double layer repulsion and van der Waals attraction) and Newtonian forces (e.g., buoyant weight and skeletal forces). Specific surface area is more informative than grain size for fine-grained sediments. It is intimately involved in defining plasticity, pore size, fabric, compressibility, swelling and shrinkage, hydraulic conductivity, capillary phenomena, and all forms of coupled processes. It also controls adsorption and retardation during advective-diffusive-reactive transport, geophysical parameters such as electrical conductivity and permittivity, and it is critical to industrial applications such as mineral separation by froth flotation or magnetic/electrical processes. Clearly, routine geotechnical characterization should include specific surface area measurements for fine-grained sediments.

Table 1 summarizes current specific surface area measurement methods, including the common dye adsorption method using either spectrometers or filter paper. Overall, these methods have ill-defined end points, are time-consuming, require expensive devices, use dry procedures (inadequate for swelling clays), or do not support detailed physical analysis.

The recent developments in sensors and cellphone technology have brought affordable solutions to all engineering areas. In particular, smartphones are widely available worldwide and include advanced tools for image analysis and colorimetry that are already being used in applications that span from science education (Kehoe and Penn 2013; Rice et al. 2014; Knutson et al. 2015), to spectroscopy (Scheeline 2010), bio-medical applications (Wang et al. 2011; Teengam et al. 2017; Lin et al. 2018) and soil testing (Choodum et al. 2017). This study presents a simple yet physically tractable wet-method to accurately measure the specific surface area of fine-grained soils using smartphone technology and dye adsorption driven by cation exchange.

1 2 3 4	81							
5 6 7	82	2. Underlying Concepts						
8 9 10 11 12 13 14	83	2.1. Adsorption						
	84	Uncompensated crystal boundaries and isomorphic substitution cause surface charge. Coulombic						
	85	forces attract counterions to neutralize the surface charge. In the presence of water, counterions and						
15 16	86	precipitated excess salts hydrate; the distribution of hydrated ions around the particle is predicted by						
17 18 19	87	the Helmholtz-Gouy-Chapman-Stern diffuse double layer theory.						
20 21 22	88	Dye adsorption techniques use cationic dyes, which dissociate in water to form positively charged						
22 23 24 25 26 27 28 29 30 31 32 33 34 25	89	hydrated ions. The hydrated dye ions exchange the counterions around the charged mineral surface.						
	90	Given sufficient time, hydrated dye ions bind to the mineral surface i.e., chemisorption.						
	91	Dye adsorption can be used to determine the soil specific surface in terms of the mass of the adsorbed						
	92	dye m_{dye} [g], the soil mass m_s [g], and the contact area of the dye molecule with the mineral surface						
	93	S_{dye} [m ² /molecule]. Then, the soil specific surface area S_s [m ² /g] obtained by dye adsorption is						
36 37 38	94	$S_s = \frac{1}{M_d} A_v S_{dye} \frac{m_{dye}}{m_s} \tag{1}$						
39 40	95	where other parameters involve the molar mass of the dye M_d [g/mol] and Avogadro's number is						
41 42 43 44 45 46 47 48 49 50	96	$A_v = 6.02 \times 10^{23}$ molecules/mol. The goal is to detect the mass of adsorbed dye needed to form a						
	97	monolayer around all grains before excess dye remains in the water.						
	98	Adsorption studies typically use the titration spectrometer method with dyes such as methylene blue						
	99	(Hang and Brindley 1970; Kahr and Madsen 1995; Santamarina et al. 2002; Hegyesi et al. 2017),						
51 52	100	crystal violet, methyl red, congo red and orange II dyes (Därr and Ludwig 1973; Bulut et al. 2008),						
53 54 55 56	101	or proteins such as hemoglobin (Paykov and Hawley 2013). Methylene blue molecules may adsorb						
57 58 59		5						

102 with a tilted orientation (Hegyesi et al. 2017; Duan et al. 2018). Tilting affects the contact area S_{dye} 103 assumed for the analysis and adds significant uncertainty to the computed specific surface area 104 values (Equation 1).

The pH-dependent mineral surface charge influences adsorption and protonation competes with dye-cation exchange (Hegyesi et al. 2017). In particular, clay minerals can exhibit strong affinity for cationic or anionic dyes depending on pH (Yagub et al. 2014). In general, the adsorption maximum is attained near the point of zero charge (Causserand et al. 2001; Shaw et al. 2003; Selvam et al. 2008; Ralla et al. 2010; Khan et al. 2012; Yagub et al. 2014; Postai et al. 2016). Figure 1a shows a compilation of pH-dependent dye adsorption data on clays for 3≤pH≤10. Data indicate that hemoglobin adsorption is particularly sensitive to pH changes under basic conditions, while the adsorption of crystal violet, methylene blue and rhodamine-B vary with pH changes under acidic conditions.

The adsorption rate can be diffusion-controlled (first-order kinetics - Lagergren 1898 - Table 2) or collision-limited (second-order kinetics - Ho and McKay 1999); in either case, the rate of adsorption decreases as surface coverage increases. Adsorption kinetics studies have explored the rate of dye adsorption on soils: crystal violet in kaolinite (Nandi et al. 2008), rhodamine-B in Moroccan clay (Damiyine et al. 2017), and methylene blue in fly ash (Kumar et al. 2005). Results show that dye adsorption onto soil surfaces follows second-order kinetics. Steering promotes shorter adsorption times (Nandi et al. 2008); under steering conditions, methylene blue, crystal violet and rhodamine-B reach stable conditions within ~30 minutes to one hour (Figure 1b).

Hydrated ions from excess salts compete for adsorption sites and reduce the adsorption rate. More generally, the increase of ionic strength i.e., concentration and valance, decreases the adsorption capacity due to surface charge shielding (Debye-Huckel double layer thickness - Nandi et al. 2009;

Fu et al. 2011; Damiyine et al. 2017). Therefore, soils should be washed to remove excess salts whenever possible.

The asymptotic adsorption at $t \rightarrow \infty$ is a function of the adsorbent concentration. Adsorption isotherms describe the relationship between the amount of adsorbed dye and the solution concentration at equilibrium. The shape of isotherms reflects underlying adsorption mechanisms as a function of temperature, time, and pH. The most common models for aqueous solutions are the Langmuir and Freundlich isotherms (Table 2). The Langmuir isotherm assumes a monolayer coverage, that all adsorption sites are equally probable and a second-order reaction (Langmuir 1918). The Freundlich isotherm is an empirical equation with fitting parameters that reflect the adsorption capacity and intensity (Freundlich 1906). Previous dye adsorption studies on clays report Langmuir isotherm adsorption (Kumar et al. 2005; Nandi et al. 2008; Fu et al. 2011; Damiyine et al. 2017).

2.2. Digital Image Colorimetry

Color is our perception of the different wavelengths that form light, from 400 nm for violet to 700 nm for red. Digital image colorimetry consists of image acquisition followed by the analysis of the color composition detected at each pixel.

Digital cameras use filters to separate the light intensity into red, green and blue RGB channels for each pixel. The value for each primary RGB color is an integer between 0 and 255 for 8 bits digitalization (Lin et al. 2018). The RGB is an additive color scheme, hence, the perceived color for a given pixel is a linear combination of red, green, and blue values and varies from zero (black) to full intensity (white). The reconstruction of the full-color image combines the three channels (Choodum et al. 2017).

The hue - saturation - value HSV representation is an alternative to the RGB scheme (see RGB to HSV conversion in Smith 1978). Hue H is the angle that specifies the position of the pure color on a color wheel (from 0 to 1). Saturation S describes its colorfulness, and the value V indicates the color lightness (V=0 for black). We can also measure the attenuation that light experiences as it traverses through a body, in this case the aqueous solution. The light absorbance A across a body of fixed thickness is (Beer-Lambert equation - Beer 1852): $A = -\log\left(\frac{l}{l_0}\right)$ (2)where I_0 is the incident light intensity and I is the transmitted intensity. . P.I.C. 3. **Experimental Study** We use digital image colorimetry to measure the dye concentration in water in order to detect the transition from surface adsorption to excess dye in solution. We implement the test procedure using smartphone technology. 3.1. Tested Soils This study involved 11 fine-grained soils with distinct mineralogies and specific surface area (from 1 to 600 m²/g). Table 3 summarizes their median grain size from hydrometer tests, specific surface area using the methylene blue spot test, liquid limit using the British fall cone test, and classification by sensitivity to pore fluid chemistry.

165 3.2 Selected Dyes

We tested three cationic dyes (methylene blue, crystal violet, and rhodamine-B) and a protein (hemoglobin-Sigma Aldrich) to explore the effect of molecular size and shape, adsorption time and pH effects. These molecules have different light absorption wavelengths, contact areas, and geometries (Table 4). We placed emphasis on short molecules to minimize the uncertainty associated with molecular orientation, tilt and contact area S_{dye} (Equation 1).

3.3. Devices

The experimental setup consisted of a smartphone, light panel, and a semitransparent glass used as
a light diffuser (Figure 2). Tests with rhodamine-B used a similar setup but with a green LED light
source and an orange bandpass filter to measure fluorescence (Figure 2b).

We calibrated the RGB and HSV color schemes for the four dyes using cuvettes filled with different concentrations. Figure 3 shows results for crystal violet. Light absorbance *A* exhibits a linear trend with dye concentration for the range used in this study (Figure 3a - Equation 2). RGB and HSV components increase linearly with dye concentration (Figure 3b and 3c). The value of color saturation S exhibits the highest sensitivity, thus, the rest of this study is based on color saturation S (Figure 3c).

³ 181 *3.4 Methods*

The test protocol developed to measure a soil's specific surface area consists of eight steps. (1) Prepare a high concentration dye solution: methylene blue 5 g/L, crystal violet 2 g/L, rhodamine-B 0.05 g/L and hemoglobin 5g/L. (2) Fill multiple test tubes with 1 g of a dry, previously washed soil to remove excess salts. (3) Disperse it in 10 ml of deionized water. (4) Add different aliquots of the dye solution to the various test tubes. (5) Mix and homogenize for 30 minutes using a vortex or

steering plate. (6) Centrifuge slurries in the test tubes for 10 minutes at 10000 rpm. (7) Place 3 ml of the supernatant fluids into transparent prismatic cuvettes. (8) Take a digital picture and analyze the image in terms of saturation S to determine excess dye concentration. Figure 4 shows typical results obtained for kaolinite using methylene blue. The sudden increase in saturation points to the transition between the end of adsorption and the beginning of excess dye.

193 4. Analysis

194 Consider a soil mass m_s [g] with specific surface area S_s [m²/g] mixed with a water mass m_w [g] and 195 a mass of dye solution m_d [g] at a dye concentration c_d [mol/g]. The dye concentration in the liquid 196 decreases to c_l [mol/g] as the surface coverage reaches s_c [mol/m²]. The mass conservation of dye 197 molecules implies:

 $m_d c_d = c_l(m_d + m_w) + m_s S_s s_c$ (3)

199 Let's adopt a hyperbolic function between surface coverage s_c and liquid concentration c_i :

$$s_c = \frac{M_{sc}c_l}{C_\beta + c_l} \tag{4}$$

The fitting parameter M_{sc} [mol/ m²] is the maximum possible surface coverage as the liquid concertation goes to infinite $c_{l}\rightarrow\infty$. The parameter C_{β} [mol/g] is the liquid concentration when the surface coverage is $s_{c}=M_{sc}/2$. Replacing the surface coverage in Equation 4 into the mass balance Equation 3 results in

$$m_d c_d = c_l (m_d + m_w) + m_s S_s \frac{M_{sc} c_l}{C_\beta + c_l}$$
(5)

206 This is a quadratic equation in terms of the liquid concentration c_l

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$$c_l^2(m_d + m_w) + c_l (C_\beta m_d + C_\beta m_w - c_d m_d + M_{sc} m_s S_s) - C_\beta c_d m_d = 0$$
(6)

Then, the liquid concentration c_l measured by colorimetry is the physically-admissible solution of the quadratic equation:

$$c_l = \frac{-B - \sqrt{B^2 - 4AC}}{2A} \tag{7}$$

where,

$$A = (m_d + m_w)$$

$$B = C_\beta (m_d + m_w) - c_d m_d + M_{sc} m_s S_s$$

$$C = -C_\beta c_d m_d$$
(8)

Figure 5 shows the fitted Equation 7 superimposed on the experimental data, where the specific surface area S_s is inverted for each soil. The same model parameters are used in all cases. The characteristic concentration is $C_{\beta}=1 \times 10^{-8}$ mol/g. The maximum surface coverage $M_{sc}=1.661 \times 10^{-6}$ mol/m² corresponds to the maximum packing density of crystal violet molecules on a mineral surface assuming a cross-section area of 100 Å²/molecule, which corresponds to the ~11 Å diameter of the crystal violet molecule.

5. Discussion

5.1. Specific surface area of Cation Exchange Capacity

This study advanced a colorimetry protocol to measure the specific surface area of fine-grained soils in view of engineering applications. The proposed dye-based approach is driven by cation exchange; in fact, similar concepts have been used to measure both specific surface area and cation exchange capacity (Hang and Brindley 1970; Kahr and Madsen 1995; Santamarina et al. 2002; Yukselen et al.

2008 and Hegyesi et al. 2017). Results show the influence of the molecular size and structure on adsorption and implications of specific surface determination.

5.2. Dyes – Comparison

Carefully selected dyes used under controlled adsorption conditions provide adequate estimates of the specific surface area for soil characterization. Figure 6 compares specific surface area values determined with the four dyes using colorimetry by image analysis against values obtained from the standard methylene blue spot test (filter paper and naked eye). We assumed that the contact area for the methylene blue molecule is S_{dye} =66 Å²/molecule to take tilting into consideration (Hang and Brindley 1970; Hähner et al. 1996). Hemoglobin and rhodamine-B produce considerably lower values, which may relate to their pH sensitivity, molecule shape and their rate of adsorption (see also Paykov and Hawley 2013; Damiyine et al. 2017). Additionally, organic rhodamine dyes form molecular aggregates that result in different molecular orientation with respect to plane of phyllosilicate particles, resulting in lower estimates of surface area (Bujdák and Iyi 2005).

On the other hand, crystal violet emerges as the best predictor relative to methylene blue. Furthermore, the uncertainty in the contact area for methylene blue ranges from $S_{dye}=24$ to 130 Å²/molecule; in contrast, crystal violet has a more regular shape and results in lower uncertainty from S_{dye} =120 to 168 Å²/molecule, even if the molecule tilts at higher concentrations.

5.3. Time: Rate of adsorption

Additional time-dependent measurements with crystal violet and kaolinite seek to establish a reliable test protocol in view of the importance of adsorption time (Figure 1b). Figure 7a shows colorimetry results measured for different steering times. The fitted adsorption model (Equation 7) results in specific surface area values of 5 m²/g for 1 min, 16 m²/ for 10 min, and 17 m²/g for 60 min of

steering. In agreement with previous observations, adsorption follows a second-order kinetic model(see fitted model in Figure 7b).

252 5.4. Wet vs. dry techniques

Water-based methods are ideal for platy phyllosilicates that would otherwise form face-to-face stacks and unreachable internal surfaces under dry conditions. X-ray diffraction measurements at small reflection angles $2\theta < 10^\circ$ can identify adsorption by changes in the reflection pattern with an increase in basal spacing (d-value).

Figure 8 shows XRD signatures for bentonite and associated changes in basal spacing due to clay swelling. The presence of water causes an increase in basal spacing from 9.79 Å (oven dry) to 18.02 Å; for reference, the crystalline swelling of montmorillonite results in d-values of 12.4, 15.4, 18.4, and 21.4 Å for 1, 2, 3 and 4 adsorbed monolayers (Clark et al. 1937; Ferrage et al. 2005). A further increase in water content causes a transition from crystalline to osmotic interlayer swelling and results in an amorphous XRD response (Holmboe et al. 2012).

Similarly, we measure an increase in basal spacing after the adsorption of crystal violet (see also
 Sharma et al. 2016). This observation confirms the insertion of crystal violet molecules between
 layers, thus, both internal and external surfaces are involved in adsorption.

266 **5.5.** *Limitations*

267 Our experience with a wide range of soils and marine sediments indicates that the proposed 268 colorimetry-based methodology is inadequate for soils with high organic content, oil-wet soils, and 269 soils with soluble impurities that may color the water (e.g., iron oxide content).

6. Engineering implications – Mobile App

The specific surface area of a fine grained soil ($S_s > 1m^2/g$) allows us to explain and anticipate its engineering properties. Examples follow.

6.1. Pore size and bioactivity

A first order estimate of mean pore size $d_{pore}=2e/(S_s\rho)$ shows that it is directly proportional to the void ratio *e* and inversely proportional to specific surface area S_s (based on parallel plate geometry, where ρ is the mineral mass density). The soil pore size compared to the nominal micron-size of a microorganism defines habitable pore space and determines whether bacteria remain active and motile, trapped within sediments (Rebata-Landa and Santamarina 2006; Phadnis and Santamarina 40, 2011).

6.2. Conductivity

Notably, the specific surface area determines the hydraulic conductivity: a larger surface area per unit volume implies smaller pores $d_{pore} = 2e/(S_s \rho)$, higher drag resistance along the grains surface and lower hydraulic conductivity. The Kozeny-Carman equation for tubes leads to the Hagen-Poiseuille equation for soils and highlights the relevance of specific surface area-dependent pore size on hydraulic conductivity (Chapuis 2012; Ren and Santamarina 2018). Analogous analyses show the central role of specific surface area on electrical conductivity and permittivity (Klein and Santamarina 2003; Bate and Burns 2014).

6.3. Liquid limit – Rheology

The liquid limit is a measure of the soil specific surface area and fabric. The fluid pH and ionic concentration determine fabric (Palomino and Santamarina 2005; Wang and Siu 2006), therefore,

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correlations between the liquid limit and specific surface area must take fluid chemistry into consideration (Farrar and Coleman 1967; Wetzel 1990; Muhunthan 1991). Similar observations apply to the rheology of clayey pastes (Jeong et al. 2010).

6.4. Compressibility

The sediment compressibility C_c increases with surface area, as hinted by correlations between C_c and liquid limit (Skempton and Jones 1944; Burland 1990; Terzaghi et al. 1996; Chong and Santamarina 2016). From double layer theory, the compressibility of clays C_c is a function of the specific surface (Sridharan and Jayadeva 1982; Tripathy and Schanz 2007).

6.5. Residual friction angle

Particles with high specific surface area tend to be platy such as phyllosilicates. High slenderness promotes particle alignment and segregation during extended shear deformation. Then, the residual friction angle decreases with the slenderness ratio and is inversely proportional to the specific surface area (Skempton 1985; Terzaghi et al. 1996; Mitchell and Soga 2005; Santamarina and Shin 2009).

6.6. Mobile app implementation

We developed a mobile app for smartphones to simplify image processing and facilitate colorimetry-based specific surface area determinations in routine geotechnical laboratory characterization (screenshots in Figure 9). The app is freely available from *<Note to reviewers: we will include here* the DOI for a permanent repository>.

7. Conclusions

Specific surface area is more informative than grain size for fine-grained sediments with $S_s > 1 \text{m}^2/\text{g}$. This study advanced a smartphone-based colorimetry protocol to measure the specific surface area

of fine-grained soils with a focus on engineering applications. We selected water-based methods to reach the internal surface area of platy phyllosilicates. This development required proper dye selection with emphasis on molecular structure, the identification of robust image processing strategies, and a physics-based analysis to minimize uncertainty. We have tested the new protocol using soils with three orders of magnitude difference in specific surface area. The choice of dye must take into consideration the mineral surface charge and its pH dependency, the dye molecule shape and size, the contact area of each molecule on the mineral surface, and reliable detection of color by digital photography. Crystal violet and the detection of excess dye in water using color saturation emerge as the preferred combination. The specific surface area of a soil is a critical parameter for the analysis of surface-related phenomena such as interparticle interaction and fabric, adsorption, viscous drag and reactive transport. Therefore, the specific surface area plays a critical role in engineering parameters such as pore size and bioactivity, plasticity, hydraulic conductivity, compressibility and the residual friction angle. Routine geotechnical laboratory characterization can easily incorporate the determination of specific surface area using cellphone technology. A freely available mobile app developed as part of this study simplifies image processing and analyses. Acknowledgments: Support for this research was provided by the KAUST Endowment at King Abdullah University of Science and Technology. Gabrielle E. Abelskamp edited the manuscript. Data Availability: All data generated or used during the study appear in the published article.

1 2 2						
3 4	336	References				
5 6 7 9 10 11 12 13 14 15 16	337 338	Akin, I. D., and Likos, W. J. 2014. Specific surface area of clay using water vapor and EGME sorption methods. Geotechnical Testing Journal, 37(6): 1016-1027.				
	339 340	Akin, I. D., and Likos, W. J. 2016. Single-point and multi-point water-sorption methods for speci surface areas of clay. Geotechnical Testing Journal, 39 (2): 291-300.				
	341 342	Bate, B., and Burns, S. E. 2014. Complex dielectric permittivity of organically modified bentonite suspensions (0.2–1.3 GHz). Canadian Geotechnical Journal, 51 (7): 782-794.				
	343 344	Beer, A. 1852. Determination of the absorption of red light in colored liquids. Ann. Phys. Chem, 78-88.				
17 18 19	345 346	Brunauer, S., Emmett, P. H., and Teller, E. 1938. Adsorption of gases in multimolecular layers. Journal of the American chemical society, 60 (2): 309-319.				
20 21 22	347 348	Bujdák, J., and Iyi, N. 2005. Molecular Orientation of Rhodamine Dyes on Surfaces of Layere Silicates. The Journal of Physical Chemistry B, 109 (10): 4608-4615.				
23 24 25	349 350	Bulut, E., Özacar, M., and Şengil, İ. A. 2008. Equilibrium and kinetic data and process design for adsorption of Congo Red onto bentonite. Journal of hazardous materials, 154(1-3): 613-622.				
26 27 28	351 352	Burland, J. 1990. On the compressibility and shear strength of natural clays. Géotechnique, 40 (3) 329-378.				
29 30 31	353 354	Causserand, C., Kara, Y., and Aimar, P. 2001. Protein fractionation using selective adsorption on clay surface before filtration. Journal of Membrane Science, 186 (2): 165-181.				
32 33 34 35	355 356 357	Cerato, A. B., and Luteneggerl, A. J. 2002. Determination of surface area of fine-grained soils b the ethylene glycol monoethyl ether (EGME) method. Geotechnical Testing Journal, 25 (3) 315-321.				
36 37 38	358 359	Chapuis, R. P. 2012. Predicting the saturated hydraulic conductivity of soils: a review. Bulletin c engineering geology and the environment, 71 (3): 401-434.				
39 40 41 42 43 44 45	360 361	Chong, SH., and Santamarina, J. C. 2016. Soil compressibility models for a wide stress range Journal of Geotechnical and Geoenvironmental Engineering, 142 (6): 06016003.				
	362 363 364	Choodum, A., Keson, J., Kanatharana, P., Limsakul, W., and Wongniramaikul, W. 2017. Selec pre and post blast trinitrotoluene detection with a novel ethylenediamine entrapped thin poly film and digital image colorimetry. Sensors and Actuators B: Chemical, 252 : 463-469.				
46 47 48	365 366	Clark, G., Grim, R., and Bradley, W. 1937. A study of the behavior of montmorillonite upon wetting. Zeitschrift für Kristallographie-Crystalline Materials, 97 (1-6): 216-222.				
49 50 51 52	367 368 369	Damiyine, B., Guenbour, A., and Boussen, R. (2017). Rhodamine B Adsorption on Natural and Modified Moroccan Clay with Cetyltrimethylammonium Bromide: Kinetics, Equilibrium and Thermodynamics. Journal of Materials and Environmenal Sciences, 8(3): 860-871.				
53 54 55 56	370 371	Därr, G., and Ludwig, U. 1973. Determination of the specific surface by adsorption from solution. Matériaux et Construction, 6 (3): 233-237.				
57 58		17				
59 60		https://mc04.manuscriptcentral.com/astm-gtj				

- 372 Duan, M., Wu, J., Xiong, Y., Fang, S., and Chen, J. 2018. Characterization and differentiation of the adsorption behavior of crystal violet and methylene blue at the silica/water interface using near field evanescent wave. Soft Matter, 14(36): 7516-7525.
- ⁷ 8
 ⁸ 376 Farrar, D., and Coleman, J. (1967). The correlation of surface area with other properties of nineteen British clay soils. Journal of Soil Science, **18**(1): 118-124.
- Ferrage, E., Lanson, B., Sakharov, B. A., and Drits, V. A. 2005. Investigation of smectite hydration properties by modeling experimental X-ray diffraction patterns: Part I. Montmorillonite hydration properties. American Mineralogist, 90(8-9): 1358-1374.
- Freundlich, H. 1906. Over the adsorption in solution. Journal of Physical Chemistry, **57**: 385-471.
- ¹⁶ 381 Fu, F., Gao, Z., Gao, L., and Li, D. 2011. Effective adsorption of anionic dye, alizarin red S, from aqueous solutions on activated clay modified by iron oxide. Industrial & Engineering Chemistry Research, 50(16): 9712-9717.
- 384
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- ²⁴ 387
 ²⁵ 387
 ²⁶ 388
 ²⁷ 389
 ²⁸ Hang, P. T., and Brindley, G. 1970. Methylene blue absorption by clay minerals. Determination of surface areas and cation exchange capacities (clay-organic studies XVIII). Clays and clay minerals, 18(4): 203-212.
- Hegyesi, N., Vad, R. T., and Pukánszky, B. 2017. Determination of the specific surface area of layered silicates by methylene blue adsorption: The role of structure, pH and layer charge.
 Applied Clay Science, 146: 50-55.
- 393 Ho, Y. S., and McKay, G. 1999. Pseudo-second order model for sorption processes. Process
 34 394 Biochemistry, 34(5): 451-465.
- Holmboe, M., Wold, S., and Jonsson, M. 2012. Porosity investigation of compacted bentonite using
 XRD profile modeling. Journal of Contaminant Hydrology, 128(1-4): 19-32.
- Jang, J., and Santamarina, J. 2015. Fines classification based on sensitivity to pore-fluid chemistry.
 Journal of Geotechnical and Geoenvironmental Engineering, 142(4): 06015018.
- Jang, J., and Santamarina, J. C. 2017. Closure to fines classification based on sensitivity to porefluid chemistry by Junbong Jang and J. Carlos Santamarina. Journal of Geotechnical and Geoenvironmental Engineering, 143(7): 07017013.
- 46 402 Jeong, S. W., Locat, J., Leroueil, S., & Malet, J. P. 2010. Rheological properties of fine-grained
 47 403 sediment: the roles of texture and mineralogy. Canadian Geotechnical Journal, 47(10): 1085 48 404 1100.
- Kahr, G., and Madsen, F. 1995. Determination of the cation exchange capacity and the surface area of bentonite, illite and kaolinite by methylene blue adsorption. Applied Clay Science, 9(5): 327-336.
- 56 57

45

32

1 2

1 2 3 4 5 6	408 409 410	Kehoe, E., and Penn, R. L. 2013. Introducing colorimetric analysis with camera phones and digital cameras: an activity for high school or general chemistry. Journal of Chemical Education, 90(9): 1191-1195.			
7 8 9 10 11 12 13 14 15 16 17	411 412 413	Khan, T. A., Dahiya, S., and Ali, I. 2012. Use of kaolinite as adsorbent: equilibrium, dynamics and thermodynamic studies on the adsorption of Rhodamine B from aqueous solution. Applied Clay Science, 69 : 58-66.			
	414 415	Klein, K. A., & Santamarina, J. C. 2003. Electrical conductivity in soils: Underlying phenomena. Journal of Environmental & Engineering Geophysics, 8 (4): 263-273.			
	416 417 418	Knutson, T. R., Knutson, C. M., Mozzetti, A. R., Campos, A. R., Haynes, C. L., and Penn, R. L. 2015. A fresh look at the crystal violet lab with handheld camera colorimetry. Journal of Chemical Education, 92(10): 1692-1695.			
18 19 20 21	419 420 421	Kristoffersen, A. S., Erga, S. R., Hamre, B., and Frette, Ø. 2014. Testing fluorescence lifetime standards using two-photon excitation and time-domain instrumentation: rhodamine B, coumarin 6 and lucifer yellow. Journal of Fluorescence, 24 (4): 1015-1024.			
22 23 24 25	422 423 424	Kumar, K. V., Ramamurthi, V., and Sivanesan, S. 2005. Modeling the mechanism involved durin the sorption of methylene blue onto fly ash. Journal of Colloid and Interface Science, 284 (1 14-21.			
26 27 28	425 426	Lagergren, S. 1898. About the theory of so-called adsorption of soluble substances. Sver Vetenskapsakad. Handingarl, 24: 1-39.			
29 30 31	427 428	Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. Journal of the American Chemical Society, 40 (9): 1361-1403.			
32 33 34 35	429 430 431	Lin, B., Yu, Y., Cao, Y., Guo, M., Zhu, D., Dai, J., and Zheng, M. 2018. Point-of-care testing f streptomycin based on aptamer recognizing and digital image colorimetry by smartphon Biosensors and Bioelectronics, 100: 482-489.			
37	432	Mitchell, J., and Soga, K. 2005. Fundamentals of Soil Behaviour. J. Wiley, 558 pages.			
38 39	433	Muhunthan, B 1991. Liquid limit and surface area of clays. Géotechnique, 41(1): 135-138.			
40 41 42 43	434 435 436	Nandi, B., Goswami, A., Das, A., Mondal, B., and Purkait, M. 2008. Kinetic and equilibrium studies on the adsorption of crystal violet dye using kaolin as an adsorbent. Separation Science and Technology, 43 (6): 1382-1403.			
44 45 46	437 438	Nandi, B., Goswami, A., and Purkait, M. 2009. Removal of cationic dyes from aqueous solutions b kaolin: kinetic and equilibrium studies. Applied Clay Science, 42 (3-4): 583-590.			
47 48 49	439 440	Ormerod, E., and Newman, A. 1983. Water sorption on Ca-saturated clays: II. Internal and exter surfaces of montmorillonite. Clay Minerals, 18 (3): 289-299.			
50 51 52 53 54 55	441 442	Palomino, A. M., and Santamarina, J. C. 2005. Fabric map for kaolinite: effects of pH and ioni concentration on behavior. Clays and Clay minerals, 53 (3): 211-223.			
	443 444	Park, J., and Santamarina, J. C. 2017. Revised Soil Classification System for Coarse-Fine Mixtures. Journal of Geotechnical and Geoenvironmental Engineering, 143 (8): 04017039.			
56 57					
58 59		19			
60		https://mc04.manuscriptcentral.com/astm-gtj			

- Paykov, O., and Hawley, H. 2013. A protein-retention method for specific surface area
 determination in swelling clays. Geotechnical Testing Journal, 36(4): 606-611.
- ⁶ 447 Phadnis, H., and Santamarina, J. 2011. Bacteria in sediments: pore size effects. Geotechnique Letters, 1(4): 91-93.
- ⁹ 449
 ¹⁰ 450
 ¹⁰ 451
 ¹⁰ Postai, D. L., Demarchi, C. A., Zanatta, F., Melo, D. C. C., and Rodrigues, C. A. 2016. Adsorption of rhodamine B and methylene blue dyes using waste of seeds of Aleurites Moluccana, a low cost adsorbent. Alexandria Engineering Journal, 55(2): 1713-1723.
- Ralla, K., Sohling, U., Riechers, D., Kasper, C., Ruf, F., and Scheper, T. 2010. Adsorption and separation of proteins by a smectitic clay mineral. Bioprocess and Biosystems Engineering, 33(7): 847-861.
- Rebata-Landa, V., and Santamarina, J. C. 2006. Mechanical limits to microbial activity in deep sediments. Geochemistry, Geophysics, Geosystems, 7(11): 1525-2027.
- 457
 458
 Ren, X., and Santamarina, J. 2018. The hydraulic conductivity of sediments: a pore size perspective. Engineering Geology, 233: 48-54.
- ²³ 459
 ²⁴ 460
 ²⁵ 8
 ²⁶ Rice, N. P., de Beer, M. P., and Williamson, M. E. 2014. A simple educational method for the measurement of liquid binary diffusivities. Journal of Chemical Education, **91**(8): 1185-1190.
- 461 Santamarina, J., Klein, K., Wang, Y., and Prencke, E. 2002. Specific surface: determination and relevance. Canadian Geotechnical Journal, 39(1): 233-241.
- 463 Santamarina, J., and Shin, H. 2009. Friction in granular media. Meso-scale shear physics in earthquake and landslide mechanics, Hatzor, YH, Sulem, J., Vardoulakis, I.(eds.), 157-188.
- 465 Santamarina, J. C., Klein, A., and Fam, M. A. 2001. Soils and waves: particulate materials behavior, characterization and process monitoring. Journal of Soils and Sediments, 1(2): 130-130.
 - 467 Scheeline, A. 2010. Teaching, learning, and using spectroscopy with commercial, off-the-shelf
 468 technology. Applied Spectroscopy, 64(9): 256A-268A.
- Selvam, P. P., Preethi, S., Basakaralingam, P., N.Thinakaran, Sivasamy, A., and Sivanesan, S. 2008.
 Removal of rhodamine B from aqueous solution by adsorption onto sodium montmorillonite. Journal of Hazardous Materials, 155(1): 39-44.
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- 478 Skempton, A. 1985. Residual strength of clays in landslides, folded strata and the laboratory.
 479 Geotechnique, 35(1): 3-18.
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- ³ 482 Smith, A. R. 1978. Color gamut transform pairs. ACM Siggraph Computer Graphics, **12**(3): 12-19.
- 5 483 Sridharan, A., and Jayadeva, M. 1982. Double layer theory and compressibility of clays.
 6 484 Geotechnique, 32(2): 133-144.
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- ¹³ 489 Terzaghi, K., Peck, R. B., and Mesri, G. 1996. Soil mechanics in engineering practice, John Wiley & Sons.
- 491 Tripathy, S., & Schanz, T. 2007. Compressibility behaviour of clays at large pressures. Canadian Geotechnical Journal, 44(3): 355-362.
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 Wetzel, A. 1990. Interrelationships between porosity and other geotechnical properties of slowly deposited, fine-grained marine surface sediments. Marine Geology, 92(1-2): 105-113.
- ³⁰ 501
 ³⁰ 501
 ³⁰ 502
 ³⁰ Yagub, M. T., Sen, T. K., Afroze, S., and Ang, H. M. 2014. Dye and its removal from aqueous solution by adsorption: a review. Advances in Colloid and Interface Science, **209**: 172-184.
- ³³ 503
 ³⁴ 504
 ³⁵ 504
 ³⁶ 505
 ³⁷ Yukselen, Y., and Kaya, A. 2008. Suitability of the methylene blue test for surface area, cation exchange capacity and swell potential determination of clayey soils. Engineering Geology, 102(1-2): 38-45.

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Figure 1. Dye adsorption. (a) pH-dependent between $3 \le pH \le 10$. (b) Time-dependent. Dyes: methylene blue, crystal violet, rhodamine-B and hemoglobin. (Data sources: ^bausserand et al. 2001; Shaw et al. 2003; Kumar et al. 2005; Nandi et al. 2008; Selvam et al. 2008; Ralla et al. 2010; Khan et al. 2012; Yagub et al. 2014 Postai et al. 2016; Damiyine et al. 2017; Kulkarni et al. 2017)

Geotechnical Testing Journal





Figure 2. Experimental setup. (a) Regular dyes: fixed position smartphone, cuvettes and back illumination with diffused white light source. (b) Fluorescent rhodaminedo back illumination with a green LED, and filter in front of lense. Geotechnical Testing Journal



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Figure 3. Concentration and color: dye calibration - Data shown for crystal ³⁶ ³⁷ ³⁶ ³⁶ ³⁷ ³⁶ ³⁶ ³⁷ ³⁶ ³⁷ ³⁷ ³⁶ ³⁶ ³⁷ ³⁷ ³⁶ ³⁶ ³⁶ ³⁷ ³⁷ ³⁷ ³⁶ ³⁷ ³⁶ ³⁷





Figure 4. Typical results for specific surface area measurements with the use of image analysis for a kaolinite (RP2) sample with methylene blue (MB) adsorption. Phage of test results after adsorption with color saturation S values for each concentration. Note: the sudden increase in saturation points to the transition between the end of adsorption and the beginning of excess dye in solution. The specific surface area for this kaolinite sample varies between 61 and 73 m²/g.



Figure 5. Data gathered by image analysis for specific surface area determination using crystal violet adsorption. Selected sediments: kaolinite (SA1 and RP2), aftapulgite and bentonite. Markers show data points. Continuous lines show the fitted model (Equation 7 – Fixed model parameters: $M_{sc}=1.66 \times 10^{-6} \text{ mol/m}^2$ and $C_{\beta}=1 \times 10^{-8} \text{ mol/g}$).



Figure 6. Comparison between specific surface area measurements using colorimetry by image analysis and the methylene blue spot on filter paper (computed with a $_{40}^{40}$ pntact area of a tilted molecule, S_{dye} =66 Å²/molecule).



Figure 7. Adsorption kinetics. (a) Added mass of dye vs. excess dye in water after different adsorption times (1, 10 and 60 minutes). (b) Adsorption time follows accord-order kinetics (Refer to Table 2).



Figure 8. XRD signatures for bentonite before and after water and dye adsorption. Changes in basal spacing (d-value) range from 9.79 to 18.02 Å. Water layers 0W, $\frac{1}{40}$ W, 2W and 3W corresponds to d-values of 9.56, 12.75, 15.57 and 18.85 Å. Basal spacing computed from low angles (20<10°) using Bragg's law n λ =2d sin $\frac{1}{40}$ for a source CuK α =1.54 Å.





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Figure 9. Smartphone application to determine the specific surface area using dye adsorption - Screenshots

Table 1. Specific surface measurement techniques, limitations and standards.

Method (references)	Limitations
Gas adsorption BET (Brunauer et al. 1938; ASTM B922-17, ASTM D4567 – 03, ASTM C1274-12)	A dry technique that results in phyllosilicates collapse and closed pores
Water vapor adsorption (Akin and Likos 2016; Ormerod and Newman 1983)	
Ethylene Glycol Monoethyl Ether (Cerato and Luteneggerl 2002; Akin and Likos 2014)	Accessible pores limited by adsorbate size
 Chemical adsorption from solution: Methylene blue adsorption by the spot and titration methods (ASTM C837-1634; Hang and Brindley 1970; Kahr and Madsen 1995; Santamarina et al. 2002; Hegyesi et al. 2017) Protein Adsorption (Paykov and Hawley 2013) 	Uncertainty in the contact area between the adsorbate and the adsorbent
 Indirect assessment from (Santamarina et al 2001) pore size distribution by mercury intrusion porosimetry permeability measurements others: thermal, electrical, X-ray diffraction patterns 	Accessible pores Based on constitutive models → Uncertainty propagation
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Table 2. Kinetic models and adsorption isotherms

	<u>First-order kinetics:</u> Physical adsorption (diffusion rate controlled)	Second-order kinetics: Chemisorption (reaction rate controlled)					
Kinetic models	$\frac{dq_t}{dt} = k_1(q_e - q)$	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$					
	For boundary conditions $q=0$ and $t=0$,	For boundary conditions $q=0$ and $t=0$,					
	$q = q_e(1 - e^{-k_1 t})$ where $1/k_1$ is the characteristic	$\frac{\iota}{q} = \frac{1}{k_2 q_e^2} + \frac{\iota}{q_e}$					
	time scale Langmuir:	Freundlich:					
Adsorption Isotherms	$q = q_e \frac{k_L c}{1 + k_L c}$	$\overline{\qquad} q = k_F c^n$					
Note: The adsorption capacity or uptake $q \text{ [mg/g]}$ is $q = \frac{(c_0 - c_f)}{m} V$							

	Specific	Mean grain size [µm]	Liquid Limit			Soil
Specimens	Surface S _s [m ² /g]		LL dw [%]	LL brine [%]	LL ker [%]	Classification
Silica Flour	0.5	20	31	26	28	F(F)-NL
Diatoms (CG1)	5	10	121	110	138	F(F)-HL
Red Sea Sediments	24	2.0	37	18	6	F(F)-NH
Kaolinite 1 (SA1)	34	0.36	48	52	67	F(F)-HI
Illite	56	0.5	43	-	-	-
Kaolinite 2 (RP2)	67	0.36	52	46	76	F(F)-IH
Attapulgite (Eastchem)	160	-	67	-	-	-
Bentonite 1 (Slm)	532	0.07	340	102	49	F(F)-IH
Bentonite 3 (KSA 1)	544	0.07	320	92	39	F(F)-LH
Bentonite 4 (KSA 2)	550	0.07	308	65	49	F(F)-IH
Bentonite 2 (HTC)	593	0.07	390	79	51	F(F)-IH

Table 3. Tested sediments - Properties

Note: Specific surface measured using methylene blue spot test (Santamarina et al. 2002), mean grain size from hydrometer test, liquid limit measured using the British fall cone with different pore fluids: deionized water (dw), brine and kerosene (ker) and soil classification based on sensitivity to pore fluid chemistry (Jang and Santamarina 2015; Jang and Santamarina 2017; Park and Santamarina 2017).

Dye	Methylene Blue C ₁₆ H ₁₈ ClN ₃ S	Rhodamine B C ₂₈ H ₃₁ ClN ₂ O ₃	Crystal Violet C ₂₅ N ₃ H ₃₀ Cl	$\begin{array}{c} \textbf{Hemoglobin} \\ C_{2952}H_{4664}O_{832}N_{812}S_8Fe_4 \end{array}$
Structure		H ₃ C CI CI CH ₃ H ₃ C N CI CI COOH		$H_{3}C$ H
Characteristics	S_{dye} = 25 - 130 A ² /molecule Slenderness= 1:5 M_d = 319.87 g/mol cationic water soluble absorption at 670 nm	$S_{dye} = 110 \text{ A}^{2}/\text{molecule}$ Slenderness= 1:1.6 $M_{d} = 479.016 \text{ g/mol}$ cationic water soluble absorption 554 nm fluorescence 576 nm	S_{dye} = 120 A ² /molecule Slenderness= 1:1.4 M_d = 407.986 g/mol cationic water soluble absorption 590 nm	S_{dye} = 3800 A ² / molecule Slenderness= 1:1 M_d = 68000 g/mol cationic / anionic water soluble absorption 420 nm

Sources: Shaw et al. 2003; Paykov and Hawley 2013; Kristoffersen et al. 2014

Figure 1. Dye adsorption. (a) pH-dependent between 3≤pH≤10. (b) Time-dependent. Dyes: methylene blue, crystal violet, rhodamine-B and hemoglobin. (Data sources: Causserand et al. 2001; Shaw et al. 2003; Kumar et al. 2005; Nandi et al. 2008; Selvam et al. 2008; Ralla et al. 2010; Khan et al. 2012; Yagub et al. 2014 Postai et al. 2016; Damiyine et al. 2017; Kulkarni et al. 2017)

Figure 2. Experimental setup. (a) Regular dyes: fixed position smartphone, cuvettes and back illumination with diffused white light source. (b) Fluorescent rhodamine-B dye: fixed position smartphone, front illumination with a green LED, and filter in front of lens.

Figure 3. Concentration and color: dye calibration - Data shown for crystal violet. (a) Light absorbance at 565 nm wavelength, (b) mean RGB values and (c) HSV values plotted versus crystal violet concentration. Note: Absorbance (a) and color saturation S (c) increase linearly with crystal violet concentration.

Figure 4. Typical results for specific surface area measurements with the use of image analysis for a kaolinite (RP2) sample with methylene blue (MB) adsorption. Image of test results after adsorption with color saturation S values for each concentration. Note: the sudden increase in saturation points to the transition between the end of adsorption and the beginning of excess dye in solution. The specific surface area for this kaolinite sample varies between 61 and 73 m²/g.

Figure 5. Data gathered by image analysis for specific surface area determination using crystal violet adsorption. Selected sediments: kaolinite (SA1 and RP2), attapulgite and bentonite. Markers show data points. Continuous lines show the fitted model (Equation 7 – Fixed model parameters: $M_{sc} = 1.66 \times 10^{-6} \text{ mol/m}^2$ and $C_{\beta} = 1 \times 10^{-8} \text{ mol/g}$).

Figure 6. Comparison between specific surface area measurements using colorimetry by image analysis and the methylene blue spot on filter paper (computed with a contact area of a tilted molecule, S_{dye} =66 Å²/molecule).

Figure 7. Adsorption kinetics. (a) Added mass of dye vs. excess dye in water after different adsorption times (1, 10 and 60 minutes). (b) Adsorption time follows second-order kinetics (Refer to Table 2).

Figure 8. XRD signatures for bentonite before and after water and dye adsorption. Changes in basal spacing (d-value) range from 9.79 to 18.02 Å. Water layers 0W, 1W, 2W and 3W corresponds to d-values of 9.56, 12.75, 15.57 and 18.85 Å. Basal spacing computed from low angles ($2\theta < 10^\circ$) using Bragg's law $n\lambda=2d \sin\theta$ for a source CuK $\alpha=1.54$ Å.

Figure 9. Smartphone application to determine the specific surface area using dye adsorption - Screenshots