The Measurement of Surface Areas of Some Silicates by Solution Adsorption

Oğuz İNEL, Fatma TÜMSEK
Osmangazi University, Department of Chemical Engineering,
Eskişehir-TURKEY

In this study, the adsorption from solution technique was used for the determination of surface areas of some silicate samples (bentonite, sepiolite, zeolitic tuff and kaolin). Methylene blue (MB), orthophenanthroline (OP) and p-nitrophenol (PNP) were selected as solutes.

The adsorption data was found to conform with the Langmuir equation within the concentration range studied, and Langmuir constants were determined for each of the samples.

The surface area values obtained were compared with those determined by nitrogen adsorption. Also the results were discussed with respect to the cation exchange capacities of the samples.

The specific surface area values of the samples were found to decrease in the following order:

Bentonite > Sepiolite > Zeolite > Kaolin (for MB and OP adsorption)

Sepiolite > Bentonite > Zeolite > Kaolin (for PNP and N_2 adsorption)

Key words: Surface area determination, solute adsorption, adsorption from solution.

Introduction

The specific surface area plays an important role in determining soil physical and chemical properties and therefore has a great influence on processes related to soil conservation, fertility, and pollution. The standard method for the determination of surface areas is the Brunauer-Emmett-Teller (BET) method[1], in which one determines the adsorption isotherm of any of a number of vapors or gases. Suitable adsorbates must be chemically inert, not subject to molecular sieving, and confined to the exterior of the solid, i.e., there must be no significant bulk penetration or site-specific interaction of the adsorbate with the solid. Although N_2 at 77 K is the most frequent adsorbate, the method is by no means limited to nitrogen, and a wide variety of suitable adsorbates (e.g. Kr) on the same solid yield similar results.

Although the BET method is widely used in soil science in surface area determination, one also finds reports of surface areas that are determined by the sorption of vapors that may penetrate into the interior of the bulk solid. For example, the "total surface areas" of expanding clays such as montmorillonite have been measured by the retention of ethylene glycol (EG)[2] and ethylene glycol mono ethyl ether (EGME)[3]. The differences between total surface areas by the retention method and external surface areas by the BET-N_2 method are considered to be "internal surface areas". In contrast with the BET model, these internal areas are created by the experiment, and their values may be expected to vary widely with different sorbates. The

reported surface areas of soils and minerals by the solvent retention methods may differ widely from the BET areas and from each other.

Permeametry and to a lesser extent, gas diffusion are used for comparison purposes due to their ease of operation and simplicity[4]. Surface areas may also be calculated from size distribution data and this transformation is the subject of a British Standard.

Surface areas can be determined from heats of immersion or adsorption and this technique has been greatly simplified with the introduction of the flow microcalorimeter[5].

Other adsorption techniques include adsorption from solution. This method was suggested by Giles et al.[6−8]. Adsorption studies have been described with fatty acids, aromatic acids, esters, phenols, iodine, polymers, and dyestuffs using a range of analytical techniques[9].

The use of adsorption from solution in determining surface areas is of secondary importance, but it still has the attraction that the experimental procedure is much simpler than in any method requiring a vacuum apparatus, and if routine measurements on a large number of samples are involved, it is usually much quicker.

The purpose of this paper is to compare the specific surface area values obtained by solution adsorption method with each other and with those determined by nitrogen adsorption and to discuss the results with respect to the cation exchange capacities of the samples. In this study, a monovalent cationic organic dye (methylene blue), orthophenanthroline and paranitrophenol were selected as solutes.

Methylene blue (MB):

The adsorption of MB has a long history of use as a method of surface area determination[5]; it has been adopted widely for solids of a variable nature (oxides, graphite, yeast, activate carbons, etc.)[10]. In the case of clays, the adsorption of MB onto smectite surfaces has been the subject of considerable investigation due to the utility of the phenomenon in determining the presence of smectites[11], their cation exchange capacity (CEC)[12] and surface area[13].

Orthophenanthroline (OP)

Lawrie[14] and Bower[15] reported that a method based on OP adsorption from a aqueous solution gives reliable results for some clays such as montmorillonite, illite and kaolin, but not halloysite or vermiculite. The adsorption of OP onto some clays (montmorillonite and kaolin) and some oxides was studied as a function of concentration, pH of solution and time[16], and adsorption was found to be irreversible and pH dependent.

Paranitrophenol (PNP):

Giles et al.[7] have investigated the adsorption of PNP for surface area evalution. It is normally used in aqueous solution but can be used in an organic solvent[17,18]. The method is recommended as being suitable for a wide variety of solids, both porous and nonporous, provided they either form a hydrogen bond with PNP or have aromatic nuclei. The use of PNP adsorption from aqueous solutions onto porous adsorbents such as silica gel or carbons has been queried by Sandle[19] who states that competition of water molecules for the surface will yield erroneous results. Giles agrees that complete coverage is not always obtained with certain acidic solids and recommends the use of other solvents. Padday[20] states that the accuracy of PNP is suspect since many isotherms show no clearly defined plateaux.

Experimental

Materials

The silicate samples used as adsorbents were bentonite supplied from the Uşak region, sepiolite from the Sivrihisar/Eskişehir region, zeolitic tuff (rich in clinoptilolite mineral) from the Bigadiç/Balıkesir region, and kaolin from Eczacıbaşı Vitra Seramic Factory-Bozüyük. The samples were named BT, SP, ZT and KL, respectively, and were dried at $105\,^{\circ}$C (24 h) and passed through a 200 mesh sieve.

Chemical analysis of the samples was performed in Eskişehir Cement Factory with an ARL 8680 XRF Spectrometer and the results are given in Table 1.

Table 1. Chemical analysis of the samples

%	BT	SP	KL	ZT
SiO_2	79.63	84.91	70.53	72.16
Al_2O_3	9.39	0.52	22.42	11.84
Fe_2O_3	4.94	0.47	2.93	1.21
CaO	0.80	1.56	0.92	3.51
MgO	0.36	11.89	0.29	1.47
P_2O_5	0.22	0.02	0.03	0.01
K_2O	3.50	0.21	2.36	1.86
Na_2O	0.08	0.11	0.10	-
SO_3	0.66	0.10	0.09	-
Cl^-	0.05	0.08	0.06	-
TiO_2	0.24	0.08	0.23	0.09
SrO_2	0.12	0.04	0.04	-
Mn_2O_3	0.02	0.01	0.02	0.02
Cr_2O_3	-	-	-	0.02

Cation exchange capacities of the samples were determined by NH_4^+ saturation[21] using Kjeldhal distillation and are given in Table 2.

The surface area of samples was determined by the nitrogen adsorption (B.E.T. method) with Micromeritics-Flowsorb II 2300. The measurements were performed in the laboratories of the TÜBİTAK Marmara Research Center.

The swelling property was determined by the procedure described in the literature[22,23]. The swelling capacity (=(final volume-initial volume)/initial volume $\star100$) of BT was found to be 220% and no swelling property was observed for other adsorbents as expected. Also, it was observed that on heating, the swelling water can be driven off as reversible.

MB was used as chloride salt, $C_{16}H_{18}N_3SCl.2H_2O$ and OP was used as ortho-phenanthroline hydrochloride, $C_{12}H_9N_2Cl.H_2O$. All the solutes (MB, OP and PNP) used were of analytical grade and were used without further purifications.

MB adsorption:

Portions of MB solutions (50 ml) of known initial concentrations (600 ppm for BT, 300 ppm for SP, 150 ppm for ZT, 100 ppm for KL) and varied amounts of adsorbents (0.05-0.5 g) were poured into volumetric

flasks. Analytical determinations of MB in solutions after equilibration (48 hours at 25°C) were performed by means of a Shimadzu-120-01 spectrophotometer. Optical densities were determined at 663 nm, which corresponds to the maximum absorption peak of MB "monomers". From the difference between initial and equilibrium concentrations, the amounts of MB adsorbed were calculated.

OP adsorption:

The adsorption of OP was carried out by adding 25 ml of OP solutions of different concentrations (0.5-16 mmol/L) to known amounts of adsorbents (0.15 g for BT, 0.1 g for SP, 0.2 g for ZT, 0.3 g for KL) in volumetric flasks. The flasks were shaken for 30 min and left for 24 h with occasional shaking at 25°C. Filtration followed and the filtrates were analyzed for OP.

OP was determined colorimetrically[24] from the color developed with ferrous iron in the presence of the reducing agent hydroxylamine hydrochloride and acetate buffer at pH 3.5. For spectrophotometric absorbance readings, 508 nm analytical wavelength was used.

PNP adsorption:

The known amounts of adsorbents (0.1 g for BT and SP, 0.25 g for ZT, 0.3 g for KL) were added to 10 ml of PNP solutions of different concentrations (1-40 mmol/L) in xylene (mixture of o-, m- and p-isomers) in volumetric flasks. The flasks were left for 24 hours with occasional shaking at 25°C.

For analytical determinations of PNP in solutions, a small amount of the equilibrium solution was poured in volumetric flasks containing the buffer solution at pH 12. Since the PNP is completely transferred into the water, the residual small amount of xylene can be taken off[25]. The PNP concentration was determined by measuring absorbance at 400 nm.

Results and Discussion

Adsorption isotherms:

The adsorption data were analyzed according to the Langmuir equation[1,9]:

$$\frac{C_e}{(x/m)} = \frac{1}{k.x_m} + \frac{C_e}{x_m}$$

where C_e is the equilibrium concentration of solute remaining in the solution, x/m is the quantity of solute adsorbed per unit weight of adsorbent, x_m and k are Langmuir constants. These constants are called adsorption capacity (solute monolayer capacity) and bonding energy constant, respectively.

Straight lines were fitted to the points by the method of least squares, where the slope of the regression line is $1/x_m$ and the intercept is $1/k.x_m$. The linear regression lines obtained had highly significant correlation coefficients (r), indicating a good fit to the Langmuir equation.

The adsorption isotherms and Langmuir lines are shown in Figures 1-12, and Langmuir constants are given in Table 2.
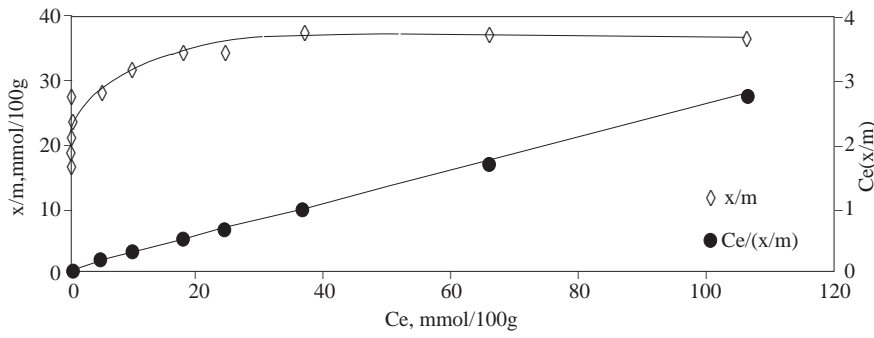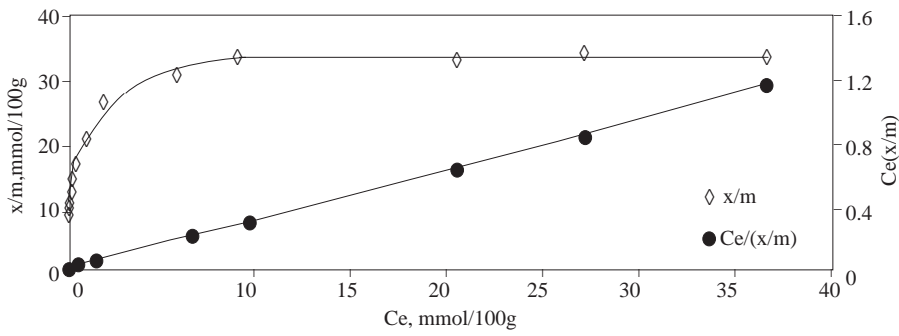
Figure 1. BT-MB adsorption isotherm and Langmuir line
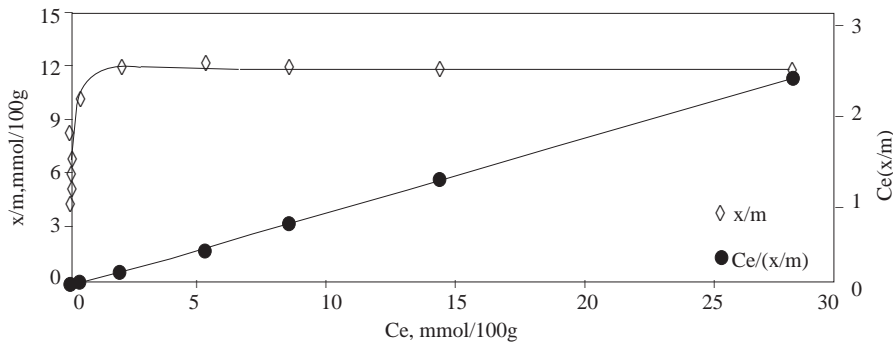

Figure 2. SP-MB adsorption isotherm and Langmuir line
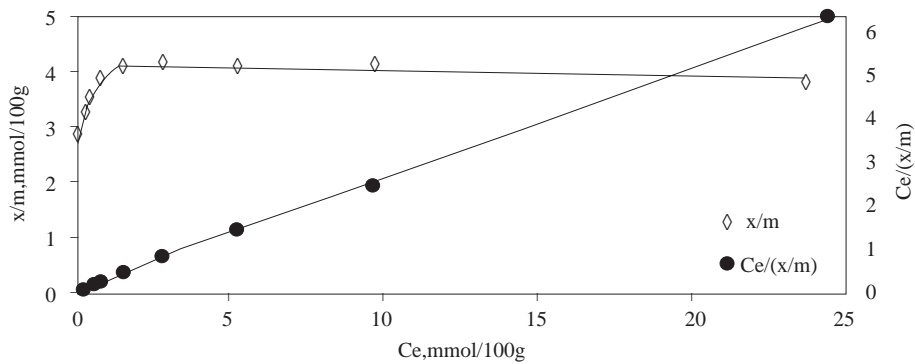

Figure 3. ZT-MB adsorption isotherm and Langmuir line

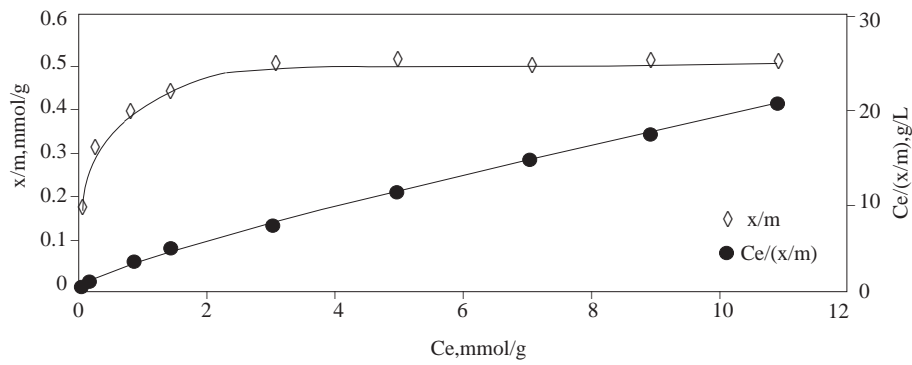**Figure 4.** KL-MB adsorption isotherm and Langmuir line
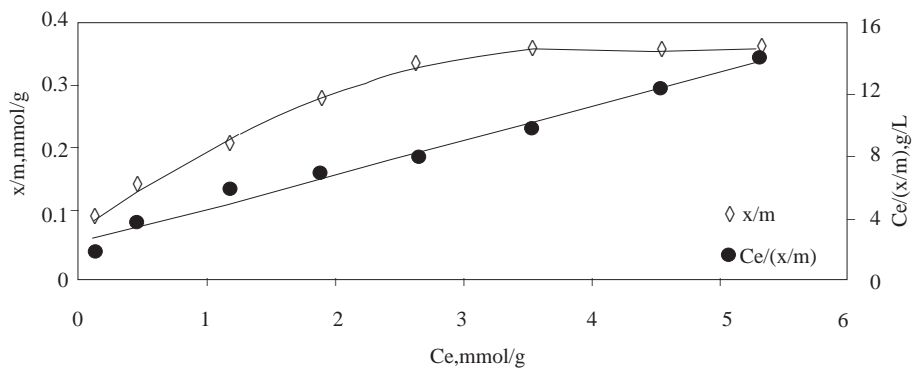
Figure 5. BT-OP adsorption isotherm and Langmuir line
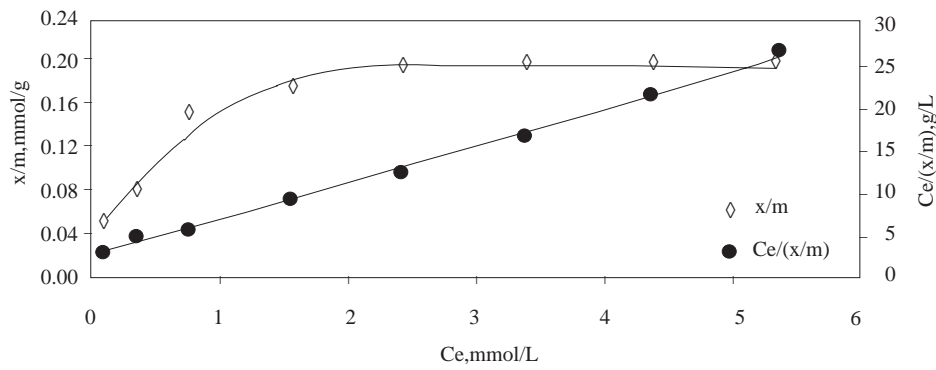
Figure 6. SP-OP adsorption isotherm and Langmuir line
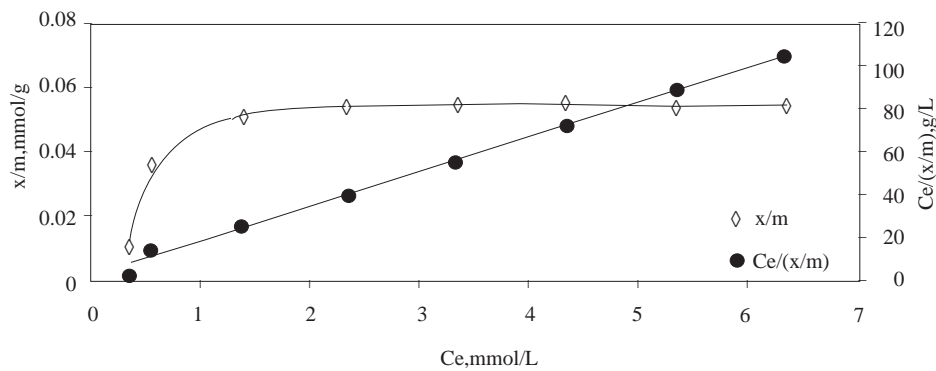
Figure 7. ZT-OP adsorption isotherm and Langmuir line
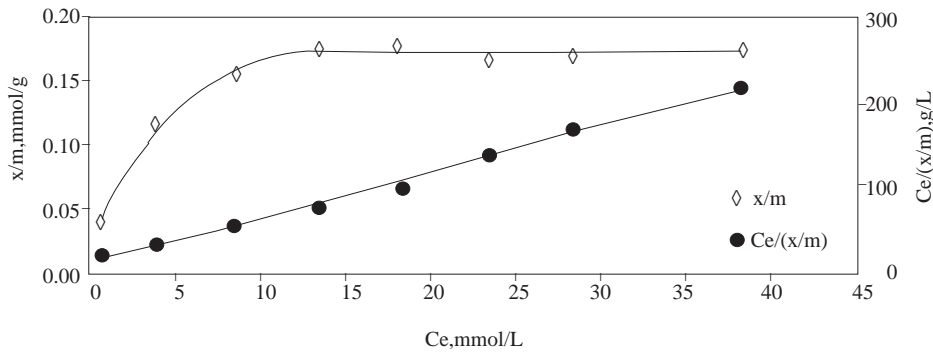
Figure 8. KL-OP adsorption isotherm and Langmuir line

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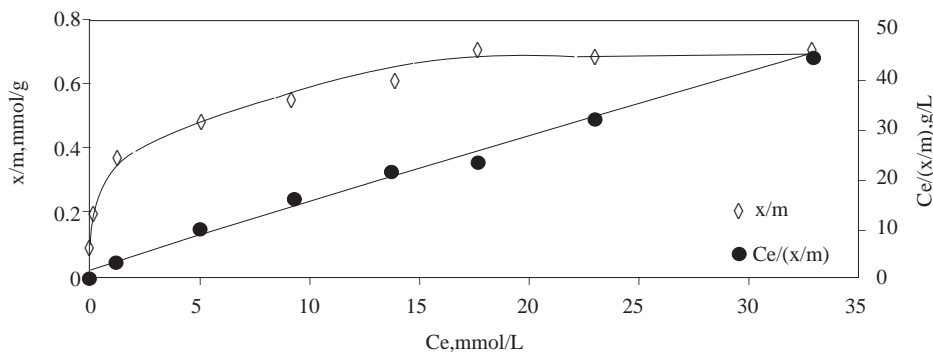**Figure 9.** BT-PNP adsorption isotherm and Langmuir line
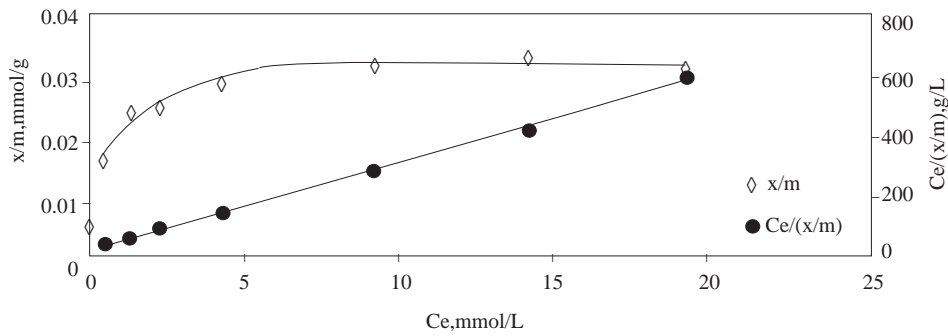

Figure 10. SP-PNP adsorption isotherm and Langmuir line

Figure 11. ZT-PNP adsorption isotherm and Langmuir line

Table 2. Langmuir constants and CEC values.

Sample	BT			SP			ZT			KL		
Adsorbate	MB	OP	PNP	MB	OP	PNP	MB	OP	PNP	MB	OP	PNP
r	0.9997	0.9997	0.9980	0.9997	0.9926	0.9961	1.0000	0.9983	0.9961	0.9997	0.9980	0.9986
k	1.2832	4.5662	0.6006	4.1855	1.2064	0.6742	244.206	2.3006	1.6214	-17.02	10.8847	0.7052
x_m	37.6648	0.5282	0.1835	32.5945	0.4342	0.7484	12.0438	0.2223	0.0336	3.9614	0.0579	0.0143
CEC (meq/100g)	31.64			6.327			94.625			5.276		

★ Unit of k is 100 g/mmol for MB and L/mmol for OP and PNP, unit of x_m is mmol/100 g for MB and mmol/g for OP and PNP.

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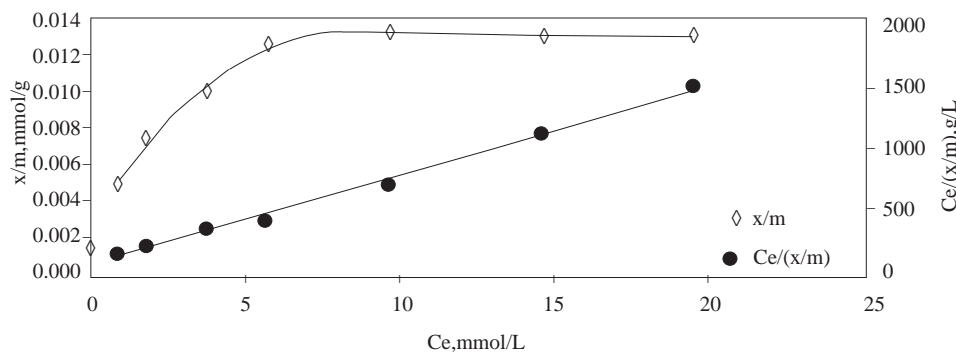

Figure 12. KL-PNP adsorption isotherm and Langmuir line

Calculation of specific surface area:

If x_m (in $mol.g^{-1}$) is the amount of solute adsorbed at monolayer per gram of adsorbent (amount of solute adsorbed at the plateau of the isotherm), A_m (in m^2) is the cross-sectional area occupied by the adsorbate unit (molecule or aggregate) on the surface and L (in mol^{-1}) is Avogadro's number; the specific surface area (in $m^2.g^{-1}$) is given by:

$$S = \frac{x_m A_m L}{N}$$

where N is the coverage factor[1,13,26].

Data in the literature regarding the size of the adsorbed MB molecule (A_m) cover rather a wide range starting from 0.60 nm^2 (sq. nanometer)(vertical-monomer) and/or 1.20 sq.nm (flat-dimer)[10,27,28] to 1.00 sq.nm[29], 1.30 sq.nm[13], 1.78 sq.nm[30] and up to 2.00 sq.nm[31]. The relatively large differences between these data are related to the variety of phenomena which may affect the adsorption of dyes on solid surfaces.

In this study, A_m values for MB, OP and PNP were taken as 1.20 sq.nm, 0.60 sq.nm[16] and 0.525 sq.nm (A_m was taken as 1.05 sq.nm for bentonite)[25], respectively.

Aggregation of MB and "coverage factor":

Polymerization reactions such as dimerizations and trimerizations are common with certain types of compounds such as cationic dyes (aggregation behavior). The monomeric and the polymeric forms of the absorbing species do not normally have identical spectra. An example of a compound which polymerizes in this manner is MB. These type of dyes are called metachromic because their colors in solution depend on concentration. At concentrations up to about 1.10^{-5} M (=3.6 ppm), the MB exists nearly completely in the monomeric form, which has an absorption maximum at a wavelength of 663 nm. At concentrations between 1.10^{-5} M and about 5.10^{-3} M, a mixture of the monomer and the dimer (absorption maximum is about 610 nm for dimeric form) is present in solution. At concentrations between about 5.10^{-3} M and about 0.1 M a mixture of the dimer and the trimer (absorption maximum is about 580 nm for trimeric form) is in solution. Above about 0.1M the MB exist nearly completely as the trimer. The variations in the absorptivities of the various forms of MB at the fixed wavelength result in a deviation from Beer's law. For MB, Beer's law is obeyed only at concentrations below about 1.10^{-5} M, where the monomer is the only polymeric form in

solution[32−34]. Unless concentration measurements of MB are made under conditions of sufficient dilutions errors will arise.

In this study, the calibration curve of the spectrophotometer (absorbance versus MB concentrations) at 663 nm was found to be linear up to 4 ppm (corresponds to absorbance of 0.8 unit) and the solutions involved were diluted to a concentration less than 4 ppm.

Giles et al.[28] found that monoionic dyes such as MB form monolayers of "ionic micelles" when they are adsorbed at a solid surface; i.e., dye ion aggregation can take place at the solid surface. The average number of dye ions per micelle (N: coverage factor) depends only on the "ionic" weight of the dye.

The coverage factor for MB is about 2. This conclusion is consistent with an adsorption mechanism which favors the flat orientation, because the dispersion forces per molecule are then maximized.

Bergmann and O'Konski[33] showed that from essentially monomeric aqueous MB solutions, MB micelles are formed at the adsorbent surface.

Kinetic and light scattering studies show that OP is adsorbed as a micellar unit composed on average of 3.5 molecules (i.e., the coverage factor of OP is 3.5)[16]. There is no micelle formation for PNP, but it was reported that the A_m value must be doubled (1.05 nm^2) when a PNP monolayer is adsorbed into the interlayer region of swelling clay minerals[25].

Comparison:

The specific surface area values of the samples (SSA) obtained by MB, OP, PNP and N$_2$ adsorption are given in Table 3.

Table 3. Specific surface areas of the samples

Sample	SSA by MB (m^2/g)	SSA by OP (m^2/g)	SSA by PNP (m^2/g)	SSA by N$_2$ (m^2/g)
BT	136	55	116	41
SP	118	45	236.5	149.5
ZT	44	23	10.6	32.46
KL	14.3	6	4.5	14

The SSA values were found to decrease in the following orders:

Bentonite>Sepiolite>Zeolite>Kaolin (for MB and OP adsorption)

Sepiolite>Bentonite>Zeolite>Kaolin (for PNP and N$_2$ adsorption)

It was found that there were relatively large differences between the SSA values obtained by solution adsorption. Taking the SSA values obtained by nitrogen adsorption as reference, SSA values for MB adsorption were found to be closer to the nitrogen surface area (except BT) than those for OP and PNP adsorption, but the SSA values of the adsorbents were found to decrease in the same order for PNP and N$_2$ adsorption. It may be more meaningful to compare the results as size sequences.

The adsorption of certain solutes from aqueous solutions was formerly considered to be physical only. It is known that with cationic solutes (MB and OP are in cationic forms; $[C_{16}H_{18}N_3S]^+$ and $[C_{12}H_9N_2]^+$, respectively, in aqueous solution) at least, cation exchange first occurs, giving way to physical adsorption only when complete replacement of the original ions (exchangeable cations in the clay structure) by cationic solute ions has occurred[11,21,35].

Although the cation exchange capacity (CEC) of zeolite is highest, it has a lower surface area than those of bentonite and sepiolite. This was attributed to "ion sieving". The system of channels and cavities

is different in each zeolite structure, giving rise to a variety of materials, each capable of screening molecules and cations by molecular or ion sieving[36]. Cation exchange takes place in the channels, but the MB or OP cations are too large to pass through entry channels of zeolite. It was therefore concluded that cationic solute adsorption by the cation exchange mechanism is rather low for zeolite and the adsorption capacity of zeolite was found to be lower than those of bentonite and sepiolite. Compared with bentonite, sepiolite has lower CEC and lower adsorption capacity. Among the adsorbents kaoline has the lowest CEC[37].

The surface area of bentonite obtained by MB and OP adsorption data was found to be higher than that obtained by nitrogen adsorption. This was attributed to the swelling property of bentonites. In liquids, montmorillonite (which is the main mineral in bentonite) sheets can be separated by penetration of liquid molecules between sheets. This leads to the characteristic swelling of montmorillonites in certain liquids, particularly in water. Because the individual sheets within the crystal can be separated in the montmorillonites, not only the external area, but also internal surface area is available.

Although the highest SSA value obtained by N_2 adsorption was for sepiolite, owing to the penetration of MB and OP cations in aqueous solutions between the sheets of the montmorillonite unit, the surface area of bentonite was found to be higher than that of sepiolite for MB and OP adsorption.

Conclusions

From the present study, the following conclusions were made:

1. All the adsorption isotherms were found to conform with the Langmuir equation.

2. The SSA values of samples obtained by PNP and N_2 adsorption were found to decrease in the following order:

Sepiolite>bentonite>zeolite>kaolin

3. The SSA values of samples obtained by MB and OP adsorption were found to decrease in the following order:

Bentonite>sepiolite>zeolite>kaolin

This discrepancy comparing with the order based on nitrogen adsorption was attributed mainly to the swelling property of bentonite.

4. Whilst experimentally simpler than the gas adsorption method, the adsorption from solution method is much more complicated on the theoretical side. Especially the variation of the cross-sectional area of the adsorbate molecule (A_m) is clearly a possible source of error in surface area determinations. Another complication is pore screening or molecular sieve effect (exclusion of adsorbate from micropores because of the large size of the solute molecules). Also, the solute molecules may be clustered into micelles on the surface of the adsorbent. Therefore, adsorption from solution method is probably reliable if only comparative values of different samples of the same material are required, but it is less reliable for absolute values.

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