A comprehensive Study on "Development of CEC Estimation Procedure Based on Specific Surface Area of Soils"

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ABSTRACT

Cation exchange capacity (CEC) is an important soil parameter of fine-grained soil. It is an effective parameter which represents the reactivity of soil, the determination of CEC is utmost importance for those soils used in many of the geoenvironmental projects. Precise determination of cation exchange capacity of soil is dependent on various soil physical properties as well as the type of cation used to determine it. Most of the CEC determination procedures reported in the literature are cumbersome and time consuming. From the detailed literature review it can be observed that the specific surface area (SSA) of soil is a significant and reliable parameter which can directly influence the value of CEC. There are simple and cost-effective methodologies for determining SSA of the soil. Therefore, an effort has been made in this study to develop simple correlations between CEC and SSA of the soil. This would help in quick and indirect estimation of CEC, reduces the cost of the experiment and the value can be usefull for a preliminary studies. A detailed database has been formulated by tabulating the values reported in the literature for CEC and SSA of soil. Based on the data base, simple regression and bilinear regression correlations are developed between CEC and SSA. These correlations were validated using measured values of different soil type. It can be observed from the validation that the general correlation for SSA gave a better estimation of CEC than the bilinear correlation. In the case of bilinear correlation, all the CEC values are over predicted. Also, SSAEGME gave a better comparison between measured and computed CEC, showing its potential for better estimation of CEC. It can also summarize from study that total surface area yields better correlations as compared to external surface area.

RÉSUMÉ

Capacité d'échange cationique (CEC) est un paramètre important du sol de sol à grains fins. C'est un paramètre efficace qui représente la réactivité du sol, la détermination de la CEC est une importance extrême pour les sols utilisé dans beaucoup de projets géoenvironnementales. Détermination précise de la capacité d'échange cationique du sol dépend de diverses propriétés physiques du sol ainsi que le type de cation utilisée pour déterminer l'il. La plupart des procédures de détermination des CEC rapportés dans la littérature sont lourdes et beaucoup de temps. De l'analyse documentaire détaillée on observe que la surface spécifique (SSA) du sol est un paramètre important et fiable qui peut influencer directement la valeur de la CEC. Il y a des méthodes simples et rentables pour déterminer la SSA du sol. Par conséquent, un effort a dans cette étude pour développer des corrélations simples entre CEC et SSA du sol. Cela aiderait à Quick et estimation indirecte de la CEC, réduit les frais de l'expérience et la valeur peut être utile pour des études préliminaires. Une base de données détaillée a été formulée par tabuler les valeurs rapportées dans la littérature pour les CEC et SSA du sol. Basée sur la régression simple, base de données et la régression bilinéaire corrélations sont développées entre CEC et SSA. Ces corrélations ont été validées à l'aide des valeurs mesurées du type de sol différentes. Elle peut être observée de la validation que la corrélation générale pour SSA a donné une meilleure estimation de la CEC que la corrélation bilinéaire. Dans le cas de corrélation bilinéaire, toutes les valeurs de la CEC sont plus prédit. En outre, SSAEGME a donné une meilleure comparaison entre CEC calculée et mesurée, montrant son potentiel pour la meilleure estimation de la CEC. Il peut également un résumé d'étude que la surface totale donne des corrélations mieux par rapport à la surface externe.

1   INTRODUCTION

CEC is a more specific parameter, compard to other soil chemical characteristic like sorption, sorption is a dependent characteristic of a particular soil-contaminant system. Therefore efficient determination of CEC is a good indicator of the reactivity of the soil. There are different methodologies adopted for measuring CEC of the soil. The precise measurement of cations is difficult due to the incomplete replacement of the cations from the cation exchange solution when measures CEC (Donald.S., 1988). Old methods to measure the CEC of soil like dilute HCl was used but its use is not always permissible as it is very likely that exchange complex itself may be destroyed (Gedroizs., 1918). Williams (1928) suggested the use of 0.5 normality acetic acid for

replacing the exchangeable cations. Kelley and Brown (1948) proposed the use of normal NH_4Cl neutralized to pH 7 with NH_4OH for determining CEC. However, most of these methods are cumbersome and tedious, which necessitates a new simple and easy methodology for CEC determination. From the past studies it can be observed that CEC of a soil is influenced by soil specific parameters like specific surface area, clay fraction, silt content, organic matter, and charge density etc. (Syers et al., 1970; Martel et al., 1978; Manrique et al., 1991). However, From the literature review it can be cleared that there is a possibility of estimation of CEC based up on soil properties like clay fraction, silt content, organic matter, charge density, specific surface area etc, Some of the researchers have also proposed a few empirical correlations for predicting the value of CEC (Seybold et al., 2006; Kaya et al., 2006). And the correlations obtained were reliable in CEC estimation. From the detailed literature review it can presumed that very limited number of studies was carried out on the relation between SSA and CEC. The study was originated to examine the relation between CEC and specific surface area. The specific surface area of the soil plays a vital role in determining reactivity of the soil because the exchange of various cations is very much dependent on the soil specific surface, based on this presumption, the present study has investigated relationship between CEC and SSA of the soil, experimentally. In addition, effort has been made to develop simple and multiple regression correlations for the quick estimation of CEC from the known soil properties of SSA. A detailed database has been formulated by tabulating the values reported in the literature for CEC and SSA of soil. Based on this, simple regression and bilinear regression correlations are developed between CEC and SSA. These correlations were validated using measured values of different soil type. It is believed that the study would be quite handy for understanding contaminant retention characteristics or reactivity of the soil more effectively and independent of the contaminant characteristics.

2   MATERIAL PROPERTIES AND METHODOLOGY

The study was carried out on two entirely different soils namely a locally available red soil (S1) and a commercially available swelling soil (S11). These soils were mixed in different proportions to obtain soils of different surface area and plasticity characteristics named as S1 to S11. These different soil mixes were used to establish correlations for CEC. In addition, 4 nos of soils (C1, C2, C3 and C4), which are entirely different from S1 and S11 were used for the validation of the proposed methodologies. The details of basic characterization of these soils are presented in table as well as in figs.

Table 1. Elemental composition of soil obtained using EDX.

Soil	Element	Amount(%)
S1	O	49.30
	Mg	0.81

Soil	Element	Amount(%)
	Al	12.93
	Si	28.26
	K	2.29
	Fe	6.30
S11	O	68.95
	Na	2.22
	Al	7.87
	Si	16.74
	Ti	0.65
	Fe	3.58

Bellow Table illustrates the experimental results for various properties of soils.

Table 2. Experimental results for Gradational, CEC and SSA of various soils

Sl. No.	Soil	Particle size			CEC (meq./100)	SSA_D (m2/g)	SSA_{EGME} (m2/g)
		Clay (%)	Silt (%)	Sand (%)			
1	S1	22	46	32	16.07	50.62	94.12
2	S2	-	-	-	24.55	53.84	108.51
3	S3	-	-	-	17.18	68.65	128.98
4	S4	-	-	-	17.96	81.58	142.64
5	S5	-	-	-	18.72	87.68	169.97
6	S6	-	-	-	19.53	92.31	187.13
7	S7	-	-	-	21.69	115.17	201.39
8	S8	-	-	-	26.54	121.92	216.35
9	S9	-	-	-	28.79	135.68	236.34
10	S10	-	-	-	31.57	168.13	264.41
11	S11	40	54	6	35.71	173.08	294.55
12	C1	40	45	15	12.14	68.22	114.89
13	C2	22	60	18	4.79	10.78	66.04
14	C3	33	55	12	7.57	21.54	45.42
15	C4	21	53	26	9.36	21.63	65.97

[1]Soil S2 to S10 are the soil obtained from mixing of S1 and S11 in different proportions as mentioned above.

3   DATA BASE STUDY

An extensive database has been formulated for CEC and SSA, based on the values reported in the literature. In the present study, CEC values and soil parameters reported by different researchers have been employed (Vanbldel et al., 1975; Gheyi et al., 1976; Barton et al., 1997; Kaya et al., 2006; Ersahin et al., 2006). It must be noted that the database includes soil from different sources with different characteristics, and hence the obtained correlation would be more general than the existing ones. However, before using the CEC values obtained from different sources, there is a need to investigate influence of different measuring methodologies on the values of soil CEC. As we observed data from Vanbldel et al., 1975 author used three different measuring methods for CEC determination, namely Ca-isotope, barium chloride, and Sodium acetate methods, gives comparable results for

majority of the soils. Based on this observation, it is understandable that CEC is an independent property of its measuring methodology. The parameters used for the analysis and its designations are listed in Table 3.

Table 3. Details of parameters used in the estimation of CEC

Parameter (P)	Unit	Symbol
SSA (EGME method) (total surface area)	m^2/g	SSA_{EGME}
SSA (N_2 method) (external surface area)	m^2/g	SSA_{N2}

The data obtained from the literature were plotted and single regression analysis has been performed to obtain equation of the form given below:

$$CEC = F(P) \qquad [1]$$

where P is the easily measurable soil property presented in Table 3.

Unlike the parameter CEC, SSA of the soil can be measured as external surface area and or total surface area (Ersahin et al., 2006; Yukslen and Kaya, 2007; Arnepalli et al., 2007). In this database study, SSA values for total surface area, and external surface area were used.

4   ANALYSIS AND VALIDATION

4.1   Analysis and Validation of Experimental Study

Analysis is carried from the results obtained CEC, SSA determined by using desiccator method (SSA_D) for external surface area and by EGME methods for total surface area. Each experiment was repeated at least thrice to ensure repeatability of results. In all the analyses, soils S1 to S11 are used for formulation of correlations and soils C1 to C4 are used for validation purpose

The results from Table 2 are plotted as depicted in Fig.1. It can be noted from the figure that a linear trend exist between CEC and SSA_D. Based on the results, a single linear regression equation for the form CEC=A+B*x has been proposed. In the equation, A and B are constants and "x" is the soil parameter such as SSA_D. The value of constants A and B are listed in Table 4. Further, close examination of Fig. 1(a) indicates that there is a considerable deviation in the data points for $SSA_D > 120$ m^2/g. Such a deviation may be attributed to the high plasticity of the soils corresponding to high SSA_D. To account this, a bilinear trend has also been proposed as shown in Fig. 1(b) and the details are listed in Table 4.
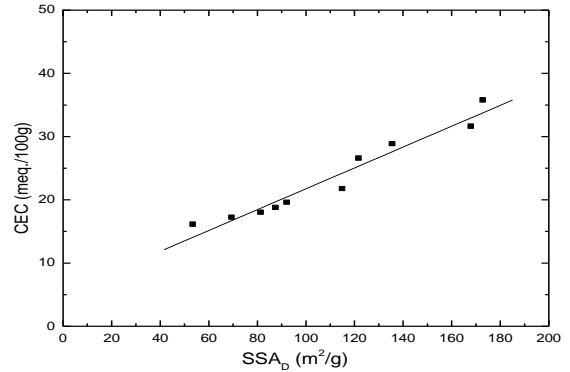

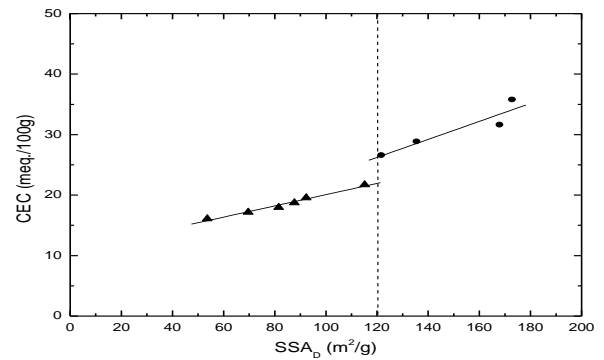Fig. 1(a) Relationship between CEC and SSA_D

Fig. 1(b) Bilinear relationship between CEC and SSA_D

The results of CEC and total SSA determined by EGME method are listed in Table 4, and the plot is depicted in Fig. 2. Similar to SSA_D, it can be noted that a linear trend exist between CEC and SSA_{EGME} and the details of the correlation obtained are presented in table 4. It can also be observed that there is a relevant deviation in the data points. Such a deviation may be attributed to the high plasticity of the soils corresponding to high SSA_{EGME}. To account this, a bilinear trend has also been proposed as shown in Fig. 2 (b) and the details are listed in Table 4.
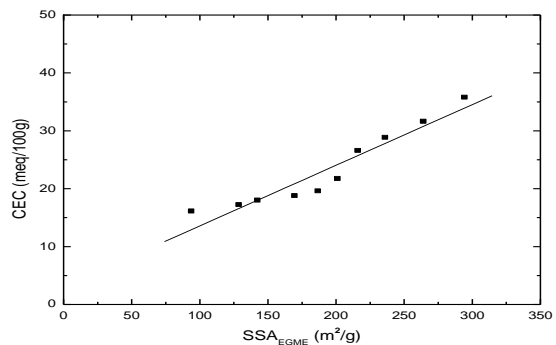

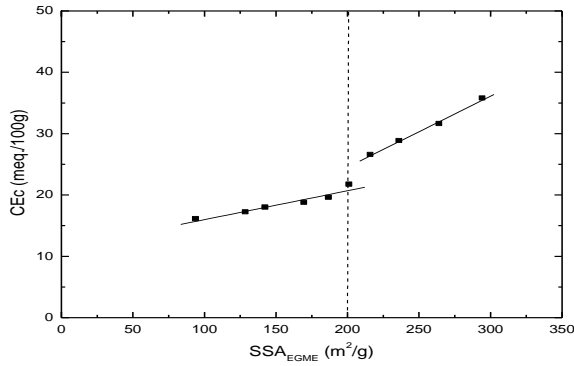Fig. 2(a) Relationship between CEC and SSA_{EGME}

Fig. 2(b) Bilinear relationship between CEC and SSA_{EGME}

The above listed single regression correlations were used to estimate CEC of C1, C2, C3, and C4 and was compared with the measured values, as depicted in Fig. 3(a) and 3(b). It can be noted from Fig. 3(a) and 3(b) that the general correlation for SSA gave a better estimation of CEC than the bilinear correlation. In the case of bilinear correlation, all the CEC values are over predicted. Also, SSA_D gave a better comparison between measured and computed CEC, showing its potential for better estimation of CEC.
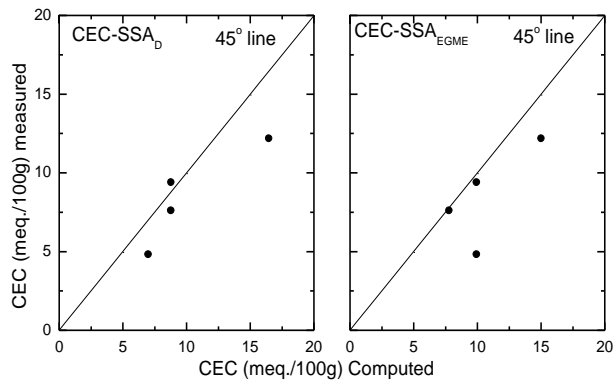

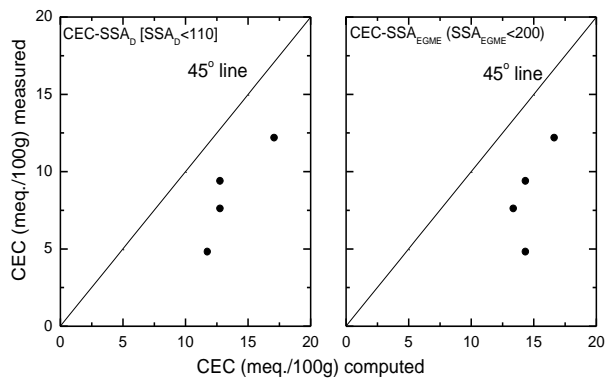Fig. 3(a) Validation of general correlation between CEC and SSA

Fig. 3(b) Validation of bilinear correlation between CEC and SSA

Table 4. Summary of single regression correlations for estimating CEC

Sl. No	Parameter (P)	Equation	Range of P	Correlation	R^2
1	SSA_D (m^2/g)	General	0-200	$0.165\ SSA_D + 5.25$	0.9740
2	SSA_D (m^2/g)	Bilinear	0-120	$0.093SSA_D + 10.79$	0.9901
			120-200	$0.148SSA_D + 8.38$	0.9352
3	SSA_{EGME} (m^2/g)	General	0-300	$0.104SSA_{EGME} + 3.09$	0.9557
4	SSA_{EGME} $(m2/g)$	Bilinear	0-200	$0.047SSA_{EGME} + 11.28$	0.9558
			200-300	$0.116SSA_{EGME} + 1.36$	0.9973

4.2   Analysis and Validation based on Data Base study

CEC of the soil has been plotted as a function of SSA_{EGME}, SSA_{MB}, SSA_{N2} as depicted in Fig. 4. It can be noted from the figures that CEC follows a good correlation with SSA_{EGME} as compared to SSA_{MB}, SSA_{N2} results. This observation matches well with those reported in the literature (Phelps and Harris, 1968; Chiacek and Bremner, 1979; Kaya and Yukselen 2006). The summary of correlations obtained were tabulated in table 5.
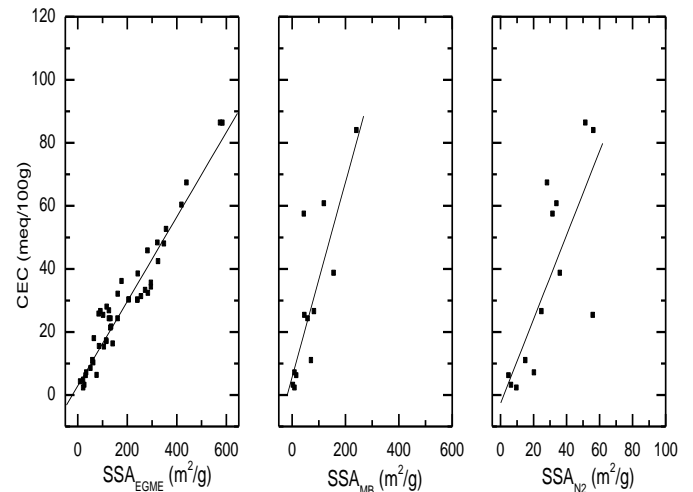

Fig. 4 Relationship between CEC and SSA obtained by using different methods

Table 5. Summary of single regression correlations for estimating CEC

Sl.No	Parameter (P)	Correlation	R^2
1	SSA_{EGME} (m^2/g)	$0.134\ SSA_{EGME} + 2.87$	0.9630
2	SSA_{MB} (m^2/g)	$0.309SSA_{MB} + 5.74$	0.8280
3	SSA_{N2} (m^2/g)	$1.33\ SSA_{N2} + 2.67$	0.7616

Based upon the results from table.5, and R^2 value the database study indicates that CEC is predominantly a function of total surface area of the soil as compared to the external surface area. Also, by knowing the value of SSA$_{EGME}$ of a soil, its CEC can be estimated easily and rapidly.

The validation is done for total surface area of these proposed relationships, i.e for SSA$_{EGME}$, with an independent data set reported in the literature (Ersahin et al., 2006, Smith et al., 1985), as depicted in Fig. 5. It can be noted that the measured and computed CEC values matches well for the obtained correlations.
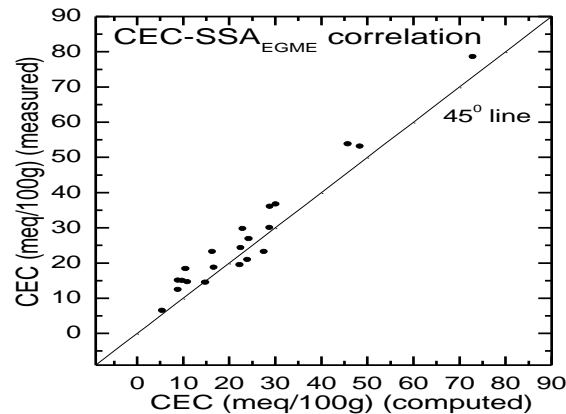

Fig. 5 Validation of general correlation between CEC and SSA

From the above validations it can be noticed that SSA$_{EGME}$ (total surface area) predominantly effects on the value of CEC. It can also be renowned that experimental data points also gave reasonably good comparison of measured and estimated CEC values indicating the robustness of this correlation.

5   CONCLUSION

The study mainly emphasizes the development of simple correlations for estimating CEC based on its specific surface area of the soil. From the rigorous study and experimental analysis it can be perceived that the soil CEC is very much dependent on the range of SSA value. Total specific surface area determined by EGME (ethylene glycol monoethyl ether) method yields a better correlation for CEC. From the study it can also be observe that The CEC value of soil mainly yields by the total surface area instead of external surface area.

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