PERFORMANCE OF LINEAR MODELS IN PREDICTING CATION EXCHANGE CAPACITY OF CALCAREOUS SOILS

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ABSTRACT

Determination of soil cation exchange capacity (CEC) in lab is cumbersome, time consuming, and costly. Accordingly, this article attempted to formulate pedotransfer functions for predicting it using some soil physical and chemical properties e.g., sand (SA), silt (SI), clay (CL), organic matter (OM) and calcium carbonate (CC). This research included four steps: preparing soil database; selecting independent variables which are related to CEC value; formulating models using NCSS 12.0.2 software, and the last step is to achieve specific objective of the research which is the comparsion among models by a series of efficiency criteria: root mean square error (RMSE), Nash-Sutcliffe model efficiency coefficient (EF), average absolute percent error (AAPE), and percentage of improving model efficiency (PIME). The statistical results of the research indicated that CEC of calcareous soils could be predicted from models that have one variable (CL), two variables (CL and OM), and three variables (CL, OM, and CC) with slight decrease in the RMSE (2.95402, 2.81180, and 2.79268) respectively, and slight increase in the EF (0.887360, 0.898448, and 0.90023) respectively. While the reliable models to predict soil CEC are formulated from the fewer number of independent variables with having the lowest points of the standardized residual of CEC that greater than +2 $cmol_c$ kg^{-1}).

Keywords: pedotransfer functions, model efficiency criteria, soil physicochemical properties.

مجلة العلوم الزراعية العراقية -2021 :52 (6):1489-1497 فتاح وكريم

أداء النماذج الخطية في التنبؤ السعة التبادلية الكاتيونية في الترب الكلسية

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المستخلص

إن تقدير السعة التبادلية الكاتيونية للتربة مختبرياً مكلف ويستغرق الكثير من الجهد والوقت ولهذا فإن الغاية من هذا البحث هو محاولة صياغة دالة للتنبؤ بها من خلال بعض الخصائص الفيزيائية والكيميائية للتربة مثل الرمل (SA) والغرين (SI) والطين (CL) والمواد العضوية (OM) وكاربونات الكالسيوم (CC). متظمنا اربع خطوات وهي: إعداد قاعدة بيانات التربة، اختيار المتغيرات المستقلة التي تتعلق بها قيم CEC، صياغة النماذج باستخدام برنامج NCSS 12.0.2، والأخيرة هي تحقيق الهدف المحدد للبحث وهو المقارنة بين النماذج من خلال سلسلة من معايير الكفاءة وهي: الجذر التربيعي لمتوسط مربعات الخطأ (RMSE)، معامل كفاءة النموذج Nash-Sutcliffe (EF)، متوسط النسبة المئوية للخطأ المطلق (AAPE)، والنسبة المئوية لتحسين كفاءة النموذج (PIME). أشارت النتائج الإحصائية للبحث إلى أن CEC للتربة الجيرية يمكن تنبؤها من خلال النماذج ذات متغير واحد (CL) ومتغيرين (CL و OM) وثلاثة متغيرات (CL و OM و CC) مع انخفاض طفيف في RMSE (2.95402 و 2.81180 و 2.79268) على التوالي، وزيادة طفيفة في EF(0.887360 و 0.898448 و 0.90023) على التوالي. ان النماذج تكون افضل للتنبؤ CEC التربة عندما تصاغ بأقل عدد من المتغيرات المستقلة مع وجود أقل عدد النقاط القياسية المتبقية المتبقية من CEC أكبر من +2 سنتي مول كغم$^{-1}$.

الكلمات المفتاحية: دوال الانتقال في التربة، معايير كفاءة النموذج، الخصائص الفيزيائية والكيميائية للتربة

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INTRODUCTION

Cation exchange capacity is the amount of negative charge on surface of soil particles (34), that is available to bind positively charged ions; cations such as (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, H^{+}, Al^{3+} and NH_4^{+}) are able of exchanging with other cations which exist on the surfaces of clay. So that fertility, nutrient retention capacity, and groundwater protection capacity against cation contamination can be indexed by soil CEC (2). Also, CEC plays an important role in soil quality (9, 16). Some researchers stated that CEC is affected by soil components. Martel *et al.*, Manrique *et al.*, Mukherjee and Zimmerman (24, 23, 27) they explained that CEC is more affected by clay, organic matter and less affected by silt. Bell and Keulen (6) showed that CEC is influenced by clay, organic carbon, and pH. While Rashidi and Seilsepour (32) exhibited that components affect CEC are sand, silt, clay, organic carbon content, as well as pH. Selecting each of these components is dependent on the quantity and its variation or homogeneity degree for example; most areas of Iraqi Kurdistan contain low organic matter, and their values are mostly homogenous. Therefore, the existence of this attribute does not affect the prediction of the CEC model. Also, the type of clay and mineralogical composition are crucial. Hepper *et al.* (14) displayed that the type of clay minerals alone could interpret up to 67% of the variation in CEC. Similarly, Martel *et al.* (24) showed that about 50% of the differences in CEC value might be due to the variations in mineralogical composition. Although changing in soil pH does not occur in the Kurdistan Region of Iraq, it is necessary to know that the CEC can directly influence the changes in soil pH, which known previously in tropical soils that have low CEC, particularly when containing a high amount of sand. In such soils, clay particles capture cations such as H^{+} and Al^{+3} which are released as a result of acidifying soils. Furthermore, minerals such as aluminum, iron, and manganese are abundant in such soils in the forms of oxides which lead to reducing CEC (10). In such cases, more investment in fertilization, especially with humic compounds is necessary (3). So such property is not necessary to be taken into consideration to predict CEC (i.e., pH does not contribute as a variation in CEC prediction models) in regions that have high buffering soil pH. There are many instances that can be used to examine the relationships among soil physical and chemical properties of modeling (e.g., determination of CEC in the soil is tedious, whereas model techniques using some physical and/or chemical soil characteristics are more economical and time saving). Cation exchange capacity is one of the most important soil properties that is required in soil databases (17, 23, 36). Estimation of CEC is difficult and expensive, particularly in regions of high $CaCO_3$ contents (calcareous soils), though it can be measured directly (11). Faraj (13) showed that the average value of calcium carbonate is more than 20% in Kurdistan region of Iraq, the locations of our study which is located in a semi-arid region. Pedotransfer functions (PTFs) consist of equations or algorithms which express the relationships between soil properties that are different either in their availability or in the complexity of their measurement (7). It can also be said that these functions solve the problems that occur between available soil data and the ones prepared for the purpose of the particular model or quality assessment. The solutions of these functions are based on computer programs for rapid prediction of that required parameter of soil, for example CEC. There are different PTF models for the estimation of CEC related to basic soil characteristics of both physical and chemical (5, 6, 8, 16, 21, 22, 23, 25, 35) but they didn't paying attention to calcareous soils. The models' results should be compared to results of specific models for predicting CEC of calcareous soils in order to evaluate their performances; low models performances need to be calibrating with a series of sensitive criteria of modeling. Therefore, the aim of this study is to formulate specific linear models to predict soil CEC that valid for a wide range of clay content in calcareous soils.

MATERIALS AND METHODS

The study of methodological included four steps: preparing the database, selecting physical and chemical properties, formulating models, and comparisons among models. Soils database have been built based on the data of the natural resources department at Sulaimani University. This database consisted of the data of 20years (1995-2015) for almost 200 different locations from agricultural farms, belong to the Kurdistan region of Iraq. The Study spots have latitude between 34°18’00” to 37°18’00”, the longitude between 42°18’00” to 46°18’00”, and the altitude ranges from 150 m at the southern boundary to more than 1800 m on the Iranian borders. The region has a semiarid climate of Mediterranean; having mild and short winter followed by a hot, dry, and long summer, the rainfall is unimodal, falling between October and May. The annual rainfall ranges from as low as 200mm at the Garmian district to as high as 800mm at the mountainous area of the Iraqi-Iranian border. There is no rainfall during the summer months. The mean annual temperature is 25 ºC with the maximum temperature of 48ºC (July) and the minimum of -10 ºC (January) (28). The soil reaction is slight to mild alkaline. The soil is non-saline; the EC of the saturation extract is below 1dS m^{-1}. With no exception, all the soils at this site are calcareous, and the lime content is usually over 20% (1). The dominant soils can be categorized under, Vertisols, Mollisols, and Inceptisols and Entisols. There are also scattered spots or red mudstone, blue marl, and chalky spots belonging to Gercus, Kolosh, and Shiranish formations (4). In general, the studied area has a wide range of clay content and low organic matter content. Data used in the study belonged to some soil physical and chemical properties in the depth of 0-30 cm, such as SA, SI, CL, OM, CC, CEC. Among the physical and chemical properties database of the soil, only properties that have related to CEC value were selected to predict the CEC. Also, standard deviation and %CV were used to select the most important independent variables in predicting soil CEC. The properties included particle size distribution which was determined by sieving and pipette methods according to the methods described by Klute *et al.* (18), total OM content applying Walkley and Black method (wet dichromate oxidation) as described by Nelson and Sommers (29), calcium carbonate contents using acid neutralization method according to Richards as described in Rowell (33), soil CEC as measured by using ammonium acetate according to Hesse (15). It is worthwhile to mention that the physical and chemical tests were made on samples passing through a 2mm sieve. Formulating models using some soil physical and chemical properties (SA, SI, CL, OM, and CC g $100g^{-1}$), twenty-seven linear regression models have been formulated by NCSS 12.0.2 statistical software, and they were classified in four different categories based on the number of independent variables, in this process, some models have not been selected which formulated from three or four parameters when all components of soil texture (SA, SI, and CL) shared in making the models that to avoid multicollinearity problems effect. Comparisons among the values of the observed soil CEC with each of the predicted soil CEC by twenty-seven models were evaluated by a series of efficiency criteria (RMSE, AAPE, EF and PIME). The model that gives the highest value of EF with the minimum value of *RMSE* and AAPE, it was considered as the best model equation for CEC predicting. The number of independent variables also took into consideration. Finally, for the best models, R^2 with equality line were plotted; the values of standardized residual versus predicted values of CEC were also plotted for the best models; the outer points indicated the numbers of samples greater than the expected frequency.

$$RMSE = \sqrt{\frac{1}{(n - df_{error})} \sum_{i=1}^{n} \left(O_i - P_i\right)^2}$$

$$AAPE = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{O_i - P_i}{O_i} \right| x100$$

$$EF = 1 - \frac{\sum_{i=1}^{n} \left(O_i - P_i\right)^2}{\sum_{i=1}^{n} \left(O_i - \overline{O}\right)^2}$$

Where: RMSE= root mean square error; AAPE= average absolute percent error; EF= Nash-Sutcliffe model efficiency coefficient. O_i= observed values; P_i= predicted values; n= number of observations; $\overline{O}$= mean of observed values.

RESULTS AND DISCUSSION

First category models

In this category, soil CEC was predicted as a function of one independent variable. As indicate in the Table 1, among the first category models (from 1 to 5), model No. 2, where *SI* considered an independent variable, had the lowest EF value 0.095272 and the highest RMSE 8.37182. The slope between them was close to a straight line; also the %CV value of *SI* was low and equal to 20.24% if compared with SA, and CL variables, as show in Table 2. However, model No. 3, where CL considered as an independent variable had the highest EF value 0.88736 with the lowest *RMSE* 2.95402 $cmol_c\ kg^{-1}$, the formula of model No. 3 is given as (CEC=11.563+0.597CL). Since it has the lowest intercept among the first category models (Table 1), model No. 3 demonstrates that the CEC value is more affected by clay content compared to the other soil properties. This might be due to that the calcareous soils have low content of organic matter and low range of pH, these lead to the most negative charges come from clay minerals. This agrees with the results obtained by Manrique *et al.*, Bell and Keulen, Noorbakhsh *et al.*, Zeraatpishe and Khormali, (23, 6, 30, 37). On the other hand, Miller (26) found that over 50% of the variation in CEC may be due to the type of *CL* alone, that agree with the current result 88.74% of CEC variation is due to clay variation. Also, Khaledian *et al*. (16) showed a positive and high significant correlation between CL and CEC (R^2 is more than 0.67 for 170 samples). A similar result was obtained before by Hepper *et al.* (14). In contrast, Rashidi and Seilsepour (31) indicate that organic carbon (OC) is the most important factor which affects soil CEC, and they used pedotransfer function in order to predict soil CEC based on soil OC as (CEC=7.93+8.72OC) which gave 74% of CEC variation was relay to OC variation for Varamin soils in Iran, respectively. Also, Khaledian *et al*. (16) showed that the effect of OM is more than the effect of CL on CEC value for Spain and USA soils, (r=0.869 and 0.859 respectively).

Table 1. Statistical parameters for multivariate linear regression of formulated models

Model category	Model No.	Intercept	Variables coefficient					Efficiency criteria	
			Sand	Silt	Clay	O.M	$CaCO_3$	RMSE	EF
One variable	1	40.340	-0.427	-	-	-	-	6.27551	0.491628
	2	46.700	-	-0.284	-	-	-	8.37182	0.095272
	3	11.563	-	-	0.597	-	-	2.95402	0.887360
	4	24.073	-	-	-	5.778	-	7.64276	0.246042
	5	42.060	-	-	-	-	-0.358	7.92829	0.188593
Two variables	6	72.684	-0.588	-0.631	-	-	-	2.93589	0.889290
	7	9.629	0.042	-	0.631	-	-	2.93589	0.889290
	8	33.289	-0.372	-	-	3.848	-	5.63085	0.592733
	9	46.354	-0.393	-	-	-	-0.269	5.61656	0.594802
	10	13.848	-	-0.042	0.588	-	-	2.93589	0.889290
	11	34.209	-	-0.198	-	5.257	-	7.43485	0.290048
	12	48.741	-	-0.168	-	-	-0.307	7.80181	0.218167
	13	10.538	-	-	0.565	1.356	-	2.81180	0.898448
	14	13.365	-	-	0.581	-	-0.050	2.92025	0.890465
	15	32.219	-	-	-	4.751	-0.266	7.15472	0.342520
Three variables	16	68.313	-0.560	-0.592	-	1.312	-	2.80332	0.899563
	17	72.476	-0.577	-0.607	-	-	-0.043	2.91488	0.891411
	18	9.094	0.032	-	0.592	1.312	-	2.80332	0.899563
	19	11.703	0.030	-	0.608	-	-0.043	2.91488	0.891411
	20	39.537	-0.356	-	-	3.094	-0.217	5.18506	0.656383
	21	12.316	-	-0.032	0.560	1.312	-	2.80332	0.899563
	22	14.758	-	-0.031	0.577	-	-0.043	2.91488	0.891411
	23	37.418	-	-0.121	-	4.559	-0.233	7.09019	0.357545
	24	12.000	-	-	0.554	1.288	-0.039	2.79268	0.900323
Fourth variables	25	68.304	-0.552	-0.575	-	1.265	-0.034	2.79193	0.900875
	26	10.752	0.023	-	0.576	1.265	-0.034	2.79193	0.900875
	27	13.090	-	-0.023	0.552	1.265	-0.034	2.79193	0.900875

Table 2. Descriptive statistics of soil physical and chemical properties of the two hundred and four soil samples used to verify soil CEC models

Descriptive Statistics	Clay	Silt ($g\ 100g^{-1}$)	Sand	Organic matter ($g\ 100g^{-1}$)	$CaCO_3$ ($g\ 100g^{-1}$)	CEC ($cmol_c\ kg^{-1}$)
Minimum	3.79	11.29	1.27	0.06	3.8	11.04
Maximum	68.41	75.66	84.92	4.69	65.01	53.87
Mean	36.46	47.07	16.47	1.60	24.42	33.31
SD	13.86	9.53	14.43	0.75	10.65	8.78
%CV	38.02	20.24	87.62	47.12	43.60	26.35

Second category models

In this category, two independent variables can be used to predict CEC. Among the second classification models (from 6 to 15), models No. 6, 10, 11, and 12, where *SI* was considered as one of the two independent variables in the models. There is a weak relationship between SI and soil CEC as mentioned in the first category. Therefore, inputting this variable in a model cannot improve the performance of estimating CEC (Table 1). Among the remaining models of this classification, two independent variables CL and OM, constitute model No. 13, which had 0.898448 as the highest EF, 2.81180 $cmol_c\ kg^{-1}$ as the lowest RMSE (CEC=10.538+0.565CL+1.356OM). This indicates that the *CL* and *OM* together has a significant impact on the cation exchange capacity. The results are coincident with those found by Drake and Motto (12) they exhibited more than 50% of differences in CEC may be due to variations in CL and OC content at several locations in New Jersey soils. A multiple linear regression was used by Majed *et al.* (22) to estimate soil CEC from CL and OM at sixty-five locations in northern Iraq; as (CEC=10.96+0.45CL+3.10OM) they summarized that 77.3% of the variation in the CEC at all soil locations could be explained by variation in CL and OM content, while the current study recorded 89.85%. Also, they concluded that the mean absolute error and standard error of measured CEC and predicted CEC are 2.713 and 2.569 $cmol_c\ kg^{-1}$, respectively this result is in agreement with our result 2.25 and 2.80 $cmol_c\ kg^{-1}$ successively. Similar results were found by Sarmadian *et al.* (35) they used pedotransfer function to evaluate soil CEC based on soil OC and CL as (CEC=1.91+0.318CL+3.96OC) with R^2=0.78 and RMSE = 6.1$cmol_c\ kg^{-1}$. Lake *et al.* (20) suggested a pedotransfer function to predict soil CEC based on soil OC and CL as (CEC=12.66+0.109CL+2.03OC) in soils in southern coastal zones of the Caspian Sea in Iran with (R^2 = 0.60).

Third category models

In this category, soil CEC was predicted as a function of three independent variables. Among the third classification models (from 16 to 24), models No. 16, 17, 21, 22, and 23, where *SI* considered as one of the three independent variables in the models. The weak relationship between *SI* and soil CEC lead to existence of this variable no avail on improving the performance of the CEC model (Table 1). Among the remaining models of this classification, model No. 24, where CL, OM, and CC considered as three independent variables had the highest *EF* value is 0.900323, and the lowest *RMSE* value is 2.79268 $cmol_c\ kg^{-1}$, which is given as (CEC=12.00+0.554CL+1.288OM–0.039CC) this might be due to that calcareous soils are alkaline and have low organic matter content, therefore, clay minerals are source of the most negative charges. In the study carried out by Bell and Keulen (6) they found that 96% of soil CEC variations were interpreted by CL, OC, and pH. While in the current study, 90% of the variation is due to CL, OM, and CC.

Fourth category models

In this category, soil CEC was predicted as a function of four independent variables. Among the fourth classification models (from 25 to 27), models No. 25 and 27, where *SI* was considered as one of the independent variables in these models which has no avail on improving the accuracy of CEC model (Table 1). In model No. 25, it notes that *SI* leads to increase intercept value which is mean increasing model error as mentioned previously in first category models. While, model No. 27 gave the same efficiency of model No. 24 which has three independent variables (CL, OM, and CC), therefore it cannot be select as one of the best models. Also, model No. 26 cannot be considered as a best model although it had 0.900875 as the highest EF, 2.79193 $cmol_c$ kg^{-1} as the lowest RMSE value. Due to the positive sign of sand coefficient which indicates to existence of multicollinearity problem, the reason may be due to the effect of combinations SA, CL and OM (CEC=10.752+0.023 SA+0.576CL+ 1.265OM–0.034CC) since it should be negative as noted in model No. 1 (Table 1).

Best models

The acceptable models in this study are valid for calcareous soils with a wide range of clay content (4-68%) Table 2; among the acceptable models, each of 3, 13, and 24 were selected as the best models due to their high *EF* value and low RMSE value (Table, 1). In order to support these results, the soil CEC predicted by models No. 3, 13, and 24 versus the soil CEC determined by laboratory tests were plotted with the line of equality (1:1) and found they are in good agreement and highly significant when the intercept set in zero point R^2 =0.8874, 0.8984, and 0.9003 respectively that confirms the adequacy of the models (Figures 1a, 1b, and 1c). Also, the standardized residual CEC versus predicted CEC were normally distributed, and 96% of the soil *CEC* differences were expected to lie between (-2 and +2).

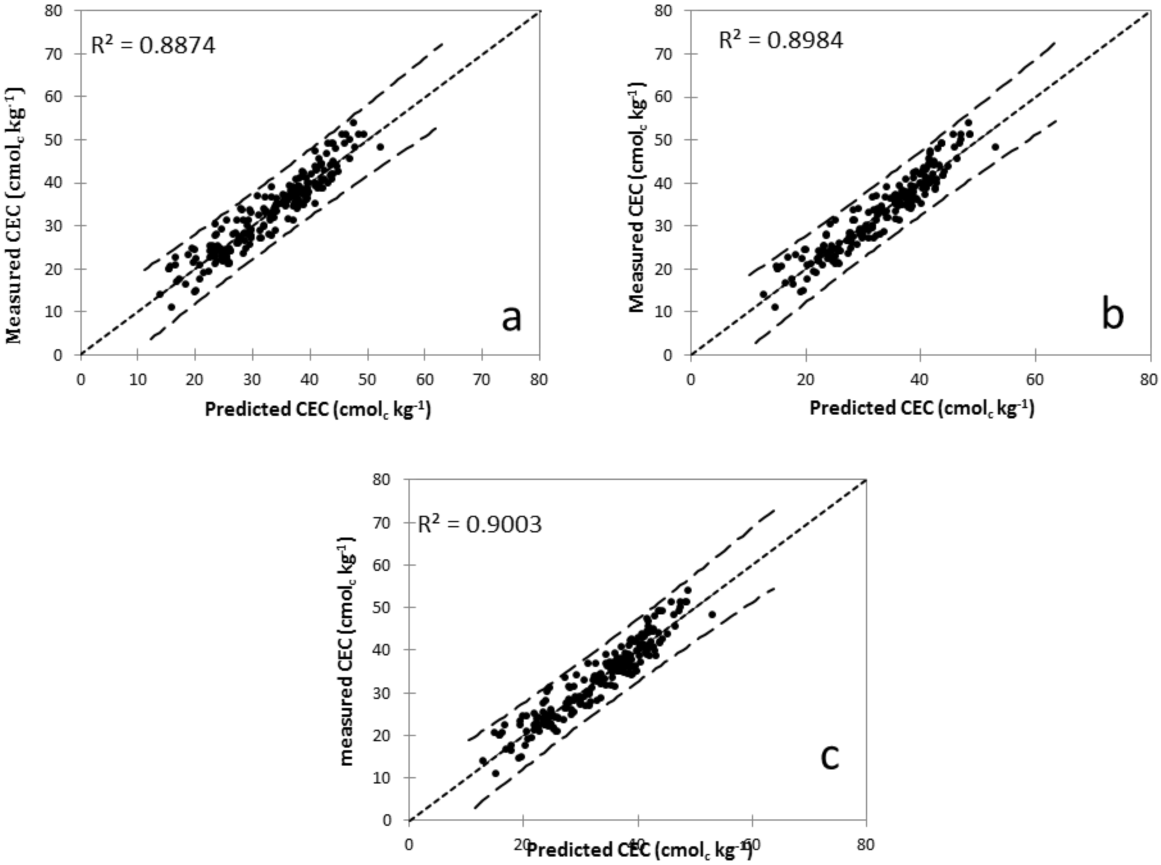

Figure 1. The scatter plots (a, b, and c) of the measured CEC versus predicted CEC using models No. (3, 13, and 24 respectively) with the line of equality (1:1)

The average absolute standardized residual CEC for models No. 3, 13, and 24 were 0.8056, 0.8003, and 0.7994 $cmol_c$ kg^{-1} (Figures 2a, 2b, and 2c) respectively. In the same figures, it was noted that models No. 3 and 13 have 4 points greater than the expected frequency (i.e., standardized residual of CEC more than +2 $cmol_c$ kg^{-1}) compared to model No. 24 that has 6 points. As well as models No. 3 and 13 have a few numbers of independent variables and a very slight difference in improving the model efficiency (1.44 and 0.21%) compared to model No. 24 (Table 3); therefore, models No. 3 and 13 can be selected as the best models for predicting CEC in calcareous soils. Thus, soil CEC predicted by model No. 3 may be 5.857 $cmol_c$ kg^{-1} lower or 6.925 $cmol_c$ kg^{-1} higher than soil CEC measured by a laboratory test. Therefore, the average absolute percent error for soil CEC prediction between model No. 3 and measured values was 7. 905%. While soil CEC predicted by model No. 13 may be 5.063 $cmol_c\ kg^{-1}$ lower or 6.011 $cmol_c\ kg^{-1}$ higher than soil CEC measured by a laboratory test. Also, the average absolute percent error for predicted soil CEC between model No. 13 and measured values was 7.397%. Therefore, Models 3 and 13 had the most reliable for prediction soil CEC when compared with the other models.

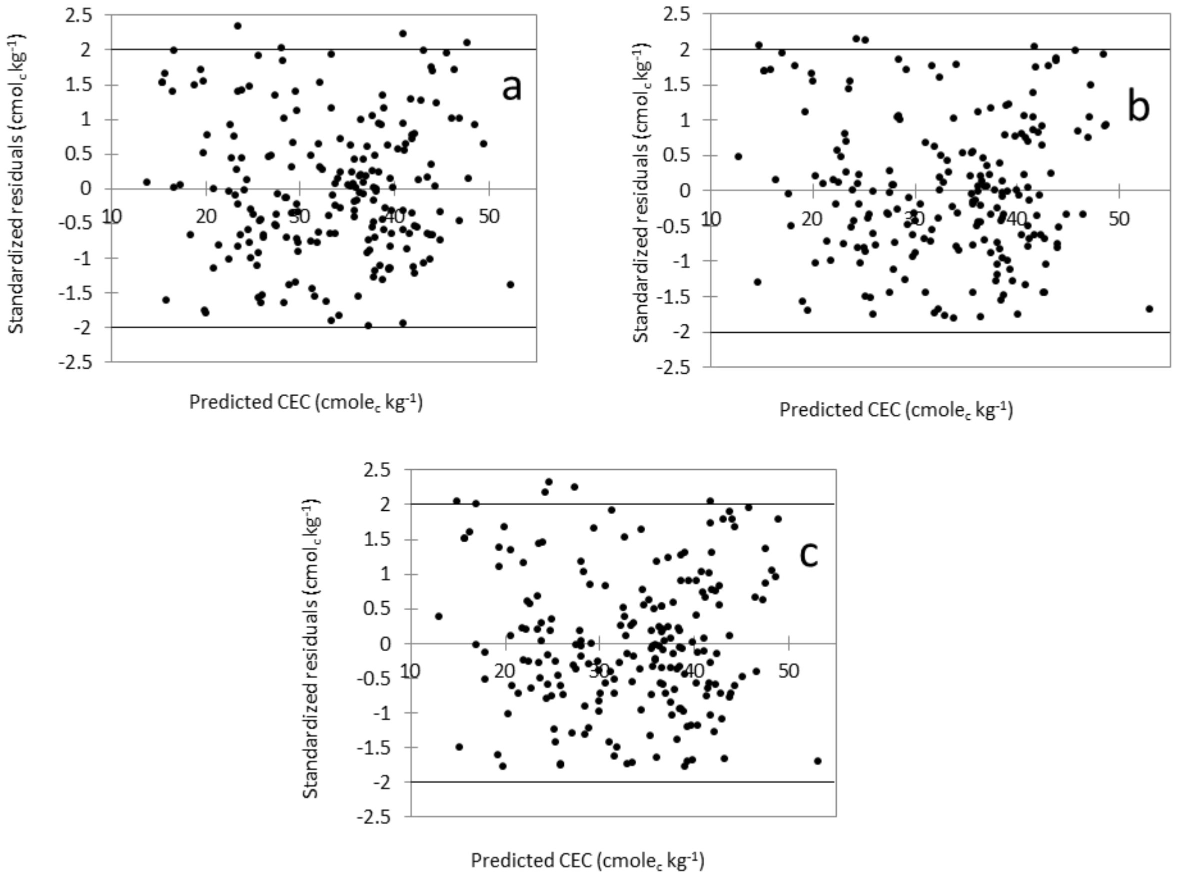

Figure 2. Plots (a, b, and c) of standardized residual CEC versus predicted CEC using models No. (3, 13, and 24, respectively).

CONCLUSION

In this study, a new pedotransfer function is formulated for predicting cation exchange capacity (CEC) in calcareous soils, based on the contents of clay, sand, silt, organic matter, and calcium carbonate. The clay content model had highest performance in estimating soil CEC compared to other single independent variables. On the other hand, the model that formulated from clay content and organic matter had the highest Nash-efficiency coefficient with the lowest RMSE and AAPE among the same category models. Comparing these two models with the one that had the highest Nash-efficiency coefficient among entire models, showed slight improvement in the efficiency model (1.44% and 0.21%) respectively, as well as these two models have fewer numbers of independent variables and standardized residual points which are more than 2$cmol_c\ kg^{-1}$. Consequently, these two models are considered more reliable for predicting CEC in calcareous soils.

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