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Article

Contribution to a Statistical Analysis of the Correlation Between the Adsorption of Heavy Metals and the Level of Carbonates in Soils

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Abstract: We have chosen hexavalent chromium as a metal for our work, Hexavalent chromium (Cr) pollution is a serious problem affecting health and the environment. This study is based on a statistical analysis applying a correlation between the level of carbonates in soils and the retention of Chromium (VI) by soil carbonates alone. The retention study was carried out using a batch method for an equilibrium time of 1h and at 23 °C on 24 soils for a limestone soil type from the soil map of the Djelfa region (Algeria), with different total limestone concentrations. The carbonates were then extracted using the Tessier (1979) procedure. Analyses indicate a significant positive linear relationship between carbonate content and chromium retention by carbonates. This relationship, confirmed by various statistical methods (Pearson correlation, Spearman rank correlation, etc.), indicates that the two variables are intrinsically correlated, implying that soil carbonates play a very important role in the retention of pollutants in soils, The results of these analyses have several important practical implications, the most important of which is for farmers to incorporate carbonate-based amendments to improve pollutant retention in soils.

Keywords: Bravais-Pearson; carbonates; Spearman; correlation; adsorption.

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1. Introduction

$Cr^{(VI)}$ soil contamination is caused by various anthropogenic activities, including mining, metallurgy, electroplating, pigment production, tanning, and wood preservation [1].

Soils behave like reservoirs of constituent pollutants, thus a potential source of pollution depending on changes in certain environmental physicochemical parameters (pH, redox potential, etc.), which then results in real environmental problems. Indeed, their leaching can cause their accumulation along food chains and thus cause public health problems [2].

Adsorption is often a surface response that plays a key role in managing the versatility of overwhelming metals in soils. The importance of adsorption as a key preparation within the versatility of overwhelming metals in soils. Adsorption is without a doubt pivotal since it includes ionic amassing at the interface between the strong and fluid stages of a medium. By lessening the concentration of overwhelming metals broken up in pore water, adsorption delays their movement into the environment [3].

It was concluded that carbonates play a part in maintaining Cr $^{(VI)}$. The calcareous soils, particularly calcite, have a partiality for the adsorption of overwhelming metals on their surface [4]. Usually reliable with past considers that affirmed the partiality of $Cr^{(VI)}$ with carbonates [5,6].

Correlation is commonly used to describe the relationship (relationship/association) between two variables. In the field of statistics, it is used to describe the relationship between two quantitative variables (generally continuous) [7].

Correlation is a statistical indicator that evaluates the correlation between two variables or sets of data [8]. This demonstrates the importance of the relationship between one variable and another variable's variation. Correlation is generally represented by a coefficient correlation, which oscillates between -1 and +1. A positive coefficient (correlation close to +1) suggests that the two variables evolve in the same direction; by increasing one, the other tends to increase and vice versa. Both variables move in opposite directions, which suggests a negative correlation (coefficient close to -1) [9].

It's crucial to understand that correlation, while a powerful tool, has its limitations. It does not allow us to determine whether there is a causal relationship between the variables. This is an important point to keep in mind when interpreting correlation results.

While correlation is a valuable tool, it's not the only one we should rely on. In general, to establish causal relationships, it is necessary to use more in-depth analytical methods, such as controlled experiments or longitudinal studies. This understanding will equip you with the necessary tools to conduct comprehensive data analysis.

2. Materials and Methods

Site description

The wilaya of Djelfa is located in the center of Algeria, limited by the Tell Atlas to the north, the Saharan Atlas to the south, and the Pre-Saharan Atlas region to the southeast. Its area is 32,256.35 square kilometers and is 300 kilometers south of the capital. It has an east longitude of 2° to 5° and a latitude of 33° to 35°. It is distinguished by its summit to the east of the Wilaya at 1613 m above sea level and its lowest point in the extreme south at 150 m above sea level [10].

Stratified sampling was carried out on 24 soil samples at a depth of 0 to 30 cm from a limestone region selected by a soil map of the wilaya of Djelfa (Figure 1). Soil samples were collected using an auger and stored in plastic bags. Each bag was meticulously labeled with the date, site number, and W 84 GPS coordinates, demonstrating our attention to detail in the study.

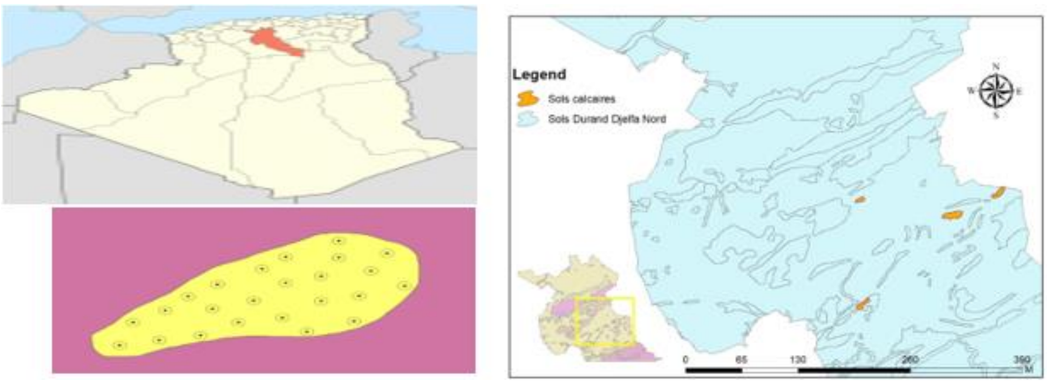

Figure 1. Situation de the study area on a type of limestone soil.

Selective extraction

Selective extractions are intended to enhance our understanding of the behavior of pollutant elements in soils, specifically their potential availability, by determining how they are distributed among various fractions extracted by a solvent (water, neutral salt, oxidizing solution, etc.) [11]. According to theory, a reagent desorbs a portion of the pollutant attached to a single soil phase, which is why extractions are referred to as selective. One of two methods can be used to desorbed hexavalent chromium: ion exchange or phase dissolution. Extraction is the process of removing the metals from the solid phases of the soil samples under study using chemicals that get stronger over time. The Tessier extraction [12] process is the most commonly utilized, and in our work, we are only interested in the percentage adsorbed and/or bonded to carbonates [13].

Phenomenon of adsorption

Adsorption is a phenomenon of accumulation of solute molecules(adsorbate) around the solid interface (adsorbent) and vice versa. Adsorption is the major process governing the mobility of heavy metals in soils. The importance of adsorption as a key process in the mobility of heavy metals in soils. Adsorption is indeed crucial, as it involves ionic accumulation at the interface between the solid and aqueous phases of a medium. By reducing the concentration of heavy metals dissolved in pore water, adsorption delays their migration in the medium [14].

Correlation coefficients

Correlation coefficients can give an overall measure of the intensity of the relationship between two traits and its significance if this relationship is monotonic.

We must calculate the correlation coefficient to estimate the intensity between two variables. Although there are several correlation coefficients, our study is based on only two [15].

citing as examples some forms of correlation coefficient

- The Brallais-Pearson linear correlation coefficient:

It's a cornerstone in statistical analysis, and plays a crucial role in determining the presence of a linear relationship between two continuous quantitative characteristics.

This coefficient allows one to determine whether there is a linear relationship between two continuous quantitative characteristics. To calculate this coefficient, you must first calculate the covariance, which is the average of the products of the deviations from the mean [16].

$$Cov(X,Y) = \frac{1}{N}\sum_{i=1}^{N}\left(X_i - \overline{X}\right) . \left(Y_i - \overline{Y}\right) \quad (1)$$

The linear correlation coefficient:

$$r(X,Y) = \frac{Cov(X,Y)}{\sigma_X . \sigma_Y} \quad (2)$$

- The Spearman rank correlation coefficient :

Analyze if there is a link between the observed ranks of the two characters; this factor is beneficial when studying a cloud of points presents a curved shape with a relationship that does not seem to be a straight line; the coefficients of Pearson are favored when the X and Y distributions are asymmetric and have exceptional values [17].

$$\rho(X,Y) = 1 - \frac{6 \cdot \sum_{i=1}^{N}\left[r(X_i) - r(Y_i)\right]^2}{N^3 - N} \quad (3)$$

Where :

r(Xi): rank of X_i in distribution.....X_1 ...X_N

r(Yi): rank of Y_i in distribution.....Y_1 ...Y_N

Forms of connection

The primary objective of this analysis is to determine the presence of a connection or pattern between the two variables. We aim to illustrate the various types of connections that can exist between 2 continuous variables:

• Positive linear connection. X and Y evolve in the same direction, an increase in X leads to an increase in Y, of the same order whatever the value of X (Graph a, Figure 2).

• Negative linear connection. X and Y move in opposite directions. The slope is stable, whatever the value of X (Graph b, Figure 2).

• Non-linear positive monotonic connection. X and Y evolve in the same direction, but the slope is different depending on the level of X (Graph c, Figure 2).

• Non-linear non-monotonic connection. A functional relationship (of sinusoidal type here) exists between X and Y. However, the relationship is not monotonic; Y can increase or decrease depending on the value of X (Graph d, Figure 2).

• Lack of connection. X's value does not indicate Y's value; they are not dependent on each other (Graph e, Figure 2).

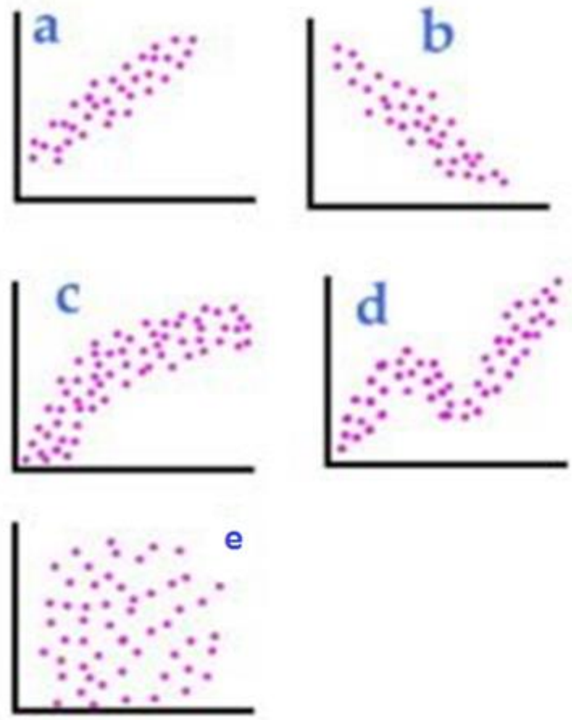

Figure 2. Some types of connection between two variables.

3. Results and Discussion

To evaluate the effect of carbonates on hexavalent chromium adsorption we opted first for a batch adsorption method at an equilibrium time of 1 hour and 23 °C, for a whole soil, then on the same soil without carbonates, and finally to compare the retention percentage obtained under the same conditions.
Extraction was carried out using a mixture of Na acetate and acetic acid (25%) at pH 4 and room temperature, the most suitable extraction method for attacking carbonates only [18].
This comparison will enable us to extract the role of carbonates in Cr(VI) retention in our soil sample.
Knowing that certain parameters essential to heavy metal retention such as CEC, and organic matter, of our samples are not very different from each other, which gives an approximate retention on these fractions, except for soil 1 which contains a higher proportion of clay than the other soils.
Soil carbonate content in % and hexavalent chromium retention on carbonates in % over the 24 points are presented in (Table 1).

Table 1. Chromium adsorption results on soils before and after carbonate phase extraction, %.

	Carbonate content	**$Cr^{(VI)}$ retention on Whole soil (Adsorption)**	**$Cr^{(VI)}$ retention on carbonate-free soil after extraction**	**$Cr^{(VI)}$ retention on extracted carbonate part**
Point 1	22.33	27.6	16.18	11.42
Point 2	27.46	32.8	15.15	17.65
Point3	19.52	18.8	7.45	11.35
Point4	18.28	22.52	10.41	12.11
Point5	23.63	28.33	12.6	15.73
Point6	14.77	19.29	9.33	9.96
Point7	18.1	29.86	19.03	10.83
Point8	25.69	31.62	14.99	16.63
Point9	18.44	23.76	12.56	11.2
Point10	16.65	21.71	12.88	8.83
Point11	10.18	18.34	11.07	7.27
Point12	9.73	14.43	8.02	6.41
Point13	23.34	32.03	17.81	14.22
Point14	25.94	26.65	10.78	15.87
Point15	12.87	27.81	18.92	8.89
Point16	24.71	25.65	10.54	15.11
Point17	17.16	22.81	12.6	10.21
Point18	21.83	26.44	15.53	10.91
Point19	9.6	21.77	14.81	6.96
Point20	27.22	29.42	11.18	18.24
Point21	27.16	32.12	12.82	19.3
Point22	19.24	24.76	11.88	12.88
Point23	25.6	24.41	7.96	16.45
Point24	21.81	21.53	9.96	11.57

Some statistical parameters of our soil samples

Table 2. Statistical soil parameters.

Parameters	The rate of carbonates	$Cr^{(VI)}$ retention on extracted carbonate part
Effective	24	24
Average	20.0525	12.4962
Standard deviation	5.64887	3.69558
Coef of variation	28.1704%	29.5735%
Minimum	9.6	6.41
Maximum	27.46	19.3
Statistical range	17.86	12.89
Asymétrie Std	-1.00552	0.360785
Flattening Std	-0.738651	-0.933085

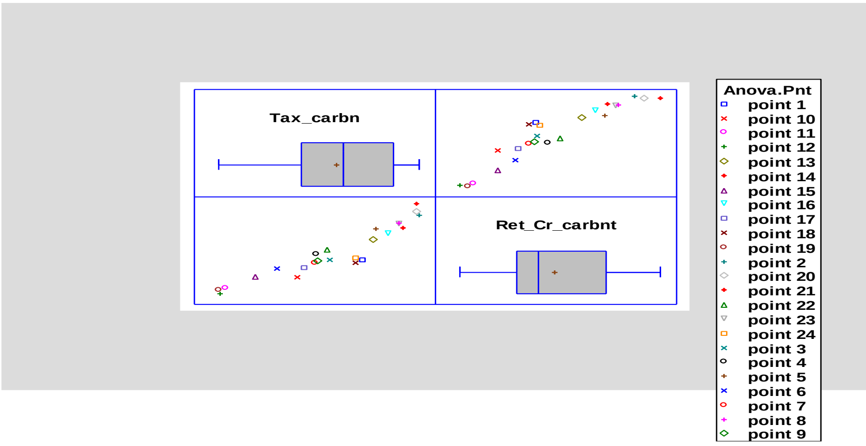

Figure 3. Scatter plots with two variables
(carbonate content % and $Cr^{(VI)}$ retention on extracted carbonate part %).

This chart displays all bivariate scatterplots for the variables selected in the analysis. Each pair of variables is displayed twice, once with the first variable on the carbonates displayed on the Y axis. All graphs in the first column display the carbonate rate variable as the most strongly correlated.

Table 3. Pearson correlation results.

Parameters	The rate of carbonate %	$Cr^{(VI)}$ retention on extracted carbonate part %
The rate of carbonates		0.9416 (24) 0.0000
Retention of $Cr^{(VI)}$	0.946 (24)	

This table provides summary statistics for each of the selected variables. It contains measures of central tendency, variability, and shape.

The standardized skewness and standardized kurtosis coefficients are of particular interest because they can be used to determine whether the sample comes from a normal distribution. Values of these statistics outside the range of -2 to +2 indicate a significant departure from normality, which could potentially render many of the statistical procedures applied to these data invalid. In this case, the following variables have standardized skewness outside the expected range, which is a point of concern.

The summary statistics play a key role in providing an overview of the distributions of the variables studied, namely carbonate content and $Cr^{(VI)}$ retention on extracted carbonate part %. The average carbonate rate is 20.0525 with a standard deviation of 5.64887, indicating moderate dispersion around the average. The standardized skew of -1.00552 suggests a slight leftward skew, but it remains within acceptable limits of normality. For $Cr^{(VI)}$ retention on extracted carbonate part %, the mean is 12.4962 with a standard deviation of 3.69558, also indicating moderate dispersion. The standardized skewness of 0.360785 indicates a slight rightward skew, with no significant deviation from normality. The coefficients of variation are identical relative variability for the two variables. These results suggest that the data for the two variables are relatively well-distributed and comparable in terms of variability.

Summary statistics indicate that the data for both variables are average and exhibit moderate variability. This allows more complex statistical analyses to continue with increased confidence in the representativeness and quality of the data.

Pearson correlation

Table 3 gives the Pearson correlations between each pair of variables. These Correlation coefficients vary between -1 and +1 and measure the strength of the linear relationship between variables. The numbers of data pairs used to calculate these coefficients are indicated in parentheses. The third number in each table box is the probability value that tests the statistical significance of the estimated correlations. Probability values below 0.05 indicate Correlation Coefficients significantly different from 0 at the 95.0% confidence level. The following pairs of variables have probability values below 0.05: Carbonate rate and Chrome retention on extracted carbonate part; the results present that the two variables have a reasonable correlation.

The Pearson correlation between carbonate content and $Cr^{(VI)}$ retention on extracted carbonate part % is 0.9416, indicating a solid positive linear relationship. The associated probability of 0.0000 means that this correlation is statistically significant at the 95% confidence level, reinforcing this observation's robustness. This strong correlation suggests that variations in carbonate content are strongly linked to $Cr^{(VI)}$ retention on extracted carbonate part %, which may be helpful for predictive analyses or process studies where these variables play a crucial role we have summarized these results in matrix form (Figure 4).

Once again, the Pearson correlation demonstrates a very strong positive and statistically significant linear relationship between carbonate content and $Cr^{(VI)}$ retention on extracted carbonate part %. This reaffirms that these two variables change in a predictable manner, which could have significant practical implications in various fields.

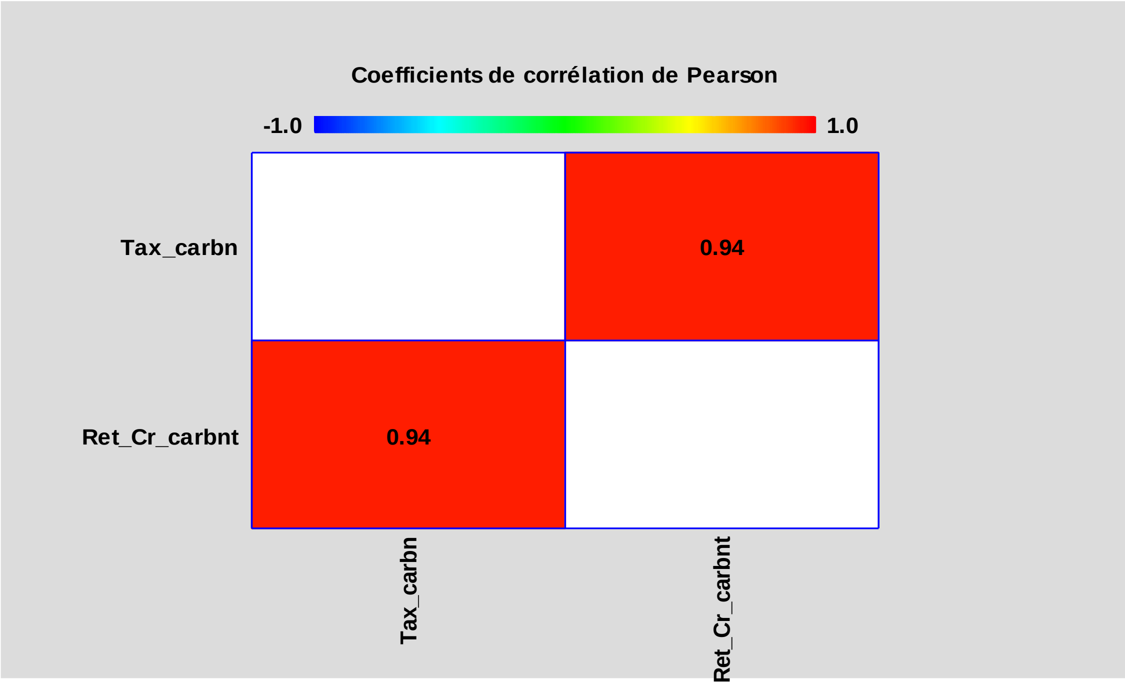

Figure 4. Pearson correlation matrix between carbonate tax and chromium retention rate.

Spearman rank correlation

Table 4. Spearman rank correlation results.

Parameters	The rate of carbonate %	$Cr^{(VI)}$ retention on extracted carbonate part %
The rate of carbonates		0.9539 (24) 0.0000
Retention of $Cr^{(VI)}$	0.9539 (24) 0.0000	

Table 4 gives the Spearman rank correlation coefficients between each pair of variables. These correlation coefficients vary between -1 and +1 and measure the strength of the association between variables. Unlike Pearson's correlation coefficients, Spearman's coefficients are calculated from the ranks of the data rather than from the data itself. Thus, they are less sensitive to extreme points than Pearson coefficients. The numbers of data pairs used to calculate these coefficients are indicated in parentheses. The third number in each table box is the probability value that tests the statistical significance of the estimated correlations.

Probability values below 0.05 indicate correlation coefficients significantly different from 0 at the 95.0% confidence level, which implies a good correlation between the two variables. The following pairs of variables have Probability values below 0.05: Carbonate Rate and Chromium Retention.

The Spearman rank correlation, at 0.9539, confirms the strong positive relationship between the carbonate content and the retention of carbonated chromium observed with Pearson. Spearman uses data ranks, which makes it less sensitive to outliers. The associated probability of 0.0000 confirms that this relationship is also statistically significant. This consistency between the two types of correlation reinforces confidence in the robustness of the observed linear relationship.

The Spearman correlation, in agreement with Pearson's, confirms a strong positive and significant relationship between the two variables. This indicates that the observed association is robust and reliable, regardless of the calculation method.

Partial correlation results

Table 5. Results of partial correlations.

Parameters	The rate of carbonate %	$Cr^{(VI)}$ retention on extracted carbonate part %
The rate of carbonates		0.9416 (24) 0.0000
Retention of $Cr^{(VI)}$	0.9416 (24) 0.0000	

Table 5 gives the partial correlation coefficients between each pair of variables. Partial correlations measure the strength of the linear relationship between variables after adjusting for the relationship with other variables. They are practical for judging the usefulness of a variable to improve the forecast of a second variable, knowing that the information provided by the other variables has already been taken into account. The numbers of data pairs used to calculate these coefficients are indicated in parentheses. The third number in each table box is the probability value that tests the statistical significance of the estimated correlations. Probability values below 0.05.

Indicate correlation coefficients significantly different from 0 at the 95.0% confidence level. The following pairs of variables have probability values below 0.05: Carbonate Rate and Chromium Retention. The results present that the two variables present good partial cooperation.

After adjusting for the effects of other variables, the partial correlation of 0.9416 maintains a robust linear relationship between carbonate content and $Cr^{(VI)}$ retention on extracted carbonate part %. The associated probability of 0.0000 presents that this relationship remains statistically significant. Partial correlations help understand direct relationships between two variables, independent of the influence of other variables.

The partial correlation confirms that the direct relationship between carbonate content $Cr^{(VI)}$ retention on extracted carbonate part **%** remains solid and significant, even after adjustment for other variables. This indicates a robust intrinsic relationship between the two main variables.

Covariance results

Table 6. Point covariance results.

Parameters	The rate of carbonate %	$Cr^{(VI)}$ retention on extracted carbonate part %
The rate of carbonates	31.9097 (24)	19.657 (24)
Retention of $Cr^{(VI)}$	19.657 (24)	13.6573 (24)

Table 6 presents the estimated covariances between each pair of variables. Covariances measure common variations between variables and are used to calculate Pearson correlations. The number of data pairs used to calculate these coefficients is presented in brackets.

The covariance of 19.657 between carbon content and chromium carbonate retention indicates that these variables increase or decrease together. The covariance measures the joint variation of the two variables, and a positive value confirms a direct relationship. However, covariance, in contrast to correlation, is not standardized, so its absolute value is less intuitive without reference to the scale of the variables. The positive covariance between carbon content and chromium carbonate retention reinforces the observation of a direct relationship where the two variables tend to increase or decrease together.

4. Conclusions

Understanding the relationship between these variables can help optimize manufacturing or processing processes where carbonate content and $Cr^{(VI)}$ retention on extracted carbonate part % play a critical role. Precise adjustments to operational conditions can be made to achieve desired results more efficiently. Additionally, these results can guide future studies and research and development (R&D) efforts to improve formulations or treatments based on these parameters. For example, additional tests can be conducted to explore how other variables influence this relationship and to develop more sophisticated optimization methods. A sorption analysis was carried out on our soil samples, extracting the carbonates and comparing chromium retention in whole soils. This confirmed the importance of carbonates in $Cr^{(VI)}$ retention. As carbonate content increases, so does $Cr^{(VI)}$ retention. This relationship, confirmed by different statistical methods, indicates that these two variables are intrinsically linked. The practical implications of these results are wide-ranging, from predictive modeling to optimizing industrial processes, optimizing soil management to maintain an appropriate level of carbonates, developing remediation strategies that exploit the ability of carbonates to retain pollutants in soils, integrating carbonate-based amendments to improve pollutant retention, and raising farmers awareness of the importance of carbonates in soils.

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