

Original article

Study of Chromium Bioavailability Using Different Extractants in Different Agricultural Soils in Libya (Tarhuna District)

Enageh Abdalgader^{*1} , Ismail Ben Sulaiman¹ , Noreeyah Alazraq² , Omar Algeidi³ ¹Department of Chemistry, Faculty of Education-Janzour, Tripoli University, Tripoli, LIBYA²Department of Chemistry, College of Science, Tarhuna, Azzaytuna University, Tarhuna, LIBYA³Department of Chemical Engineering, Faculty of Engineering, Sabratha University, LIBYAEmail: E.Abdalgader@uot.edu.ly

Abstract

Chromium (Cr) bioavailability in calcareous agricultural soils is strongly influenced by soil properties and extraction conditions, yet limited data exist for Libyan soils. This study aimed to evaluate the extractability of Cr using eight single extractants (deionized water, EDTA, ammonium acetate, ammonium chloride, ammonium oxalate, hydroxylamine HCl, calcium chloride, and magnesium chloride) at three pH values (4.91, 6.00, and 10.14) across six soils from the Tarhuna district, Libya, representing high carbonate (>30% CaCO₃) and low carbonate (<3% CaCO₃) groups. Total Cr concentrations averaged 6.03 mg/kg in low carbonate soils (0–10 cm depth) and 6.91 mg/kg in high carbonate soils (40–50 cm depth). Extractable Cr ranged from 0.0116 mg/kg (EDTA, pH 10.14) to 0.225 mg/kg (NH₄OAc, pH 10.14), corresponding to 0.17–3.73% of total Cr. Based on established Cr speciation chemistry, extraction at pH 10.14 is expected to favor solubilization of Cr(VI) anionic species, whereas acidic to neutral pH (4.91–6.00) favors release of Cr(III) species; direct speciation analysis was not performed in this study. Ammonium acetate at pH 10.14 produced the highest extraction efficiency (3.73% of total Cr), while EDTA at pH 10.14 in high-carbonate soils gave the lowest (0.17%). Extraction curves showed marked differences between high and low carbonate soils, particularly with deionized water, reflecting Cr(VI) retention by CaCO₃ under alkaline conditions. Alkaline pH (10.14) preferentially extracted Cr(VI) as anionic species, whereas acidic to neutral pH (4.91–6.00) favored Cr(III) release. Correlation analysis (n=42) revealed weak positive relationships between EDTA extractable Cr and organic matter (r up to 0.176) and weak negative relationships with CaCO₃ (r down to –0.266), indicating that other factors (e.g., clay content, oxide mineralogy) also contribute to Cr retention. Although absolute extraction values were low, the extractable Cr concentrations (0.0116 to 0.225 mg/kg) fall within ranges reported to influence plant uptake in sensitive species, suggesting potential ecological relevance under specific conditions.

Keywords. Chromium Bioavailability, Calcareous Soils, Extractants, pH Effect, Ammonium Oxalate, Libyan Agriculture.

Introduction

The assessment of trace element bioavailability in soils remains a fundamental challenge in environmental chemistry and soil fertility, as it determines the potential mobility, plant uptake, and food chain entry of both essential and potentially toxic elements [1, 2]. Bioavailability is not a single fixed value but rather a complex function of the element's chemical speciation, soil properties, and the biological receptor of interest [3, 4]. Chromium (Cr) is of particular concern because its toxicity, mobility, and bioavailability depend entirely on its chemical form: trivalent Cr(III) is relatively insoluble, forms stable complexes with organic matter, and is considered essential for mammalian metabolism in trace amounts, whereas hexavalent Cr(VI) is highly soluble, mobile, and a known human carcinogen [5, 6]. In agricultural soils, Cr originates from both natural weathering of parent materials and anthropogenic inputs such as fertilizers, sewage sludge, and industrial effluents, but its fate is strongly modulated by soil properties including pH, calcium carbonate content, organic matter, and redox conditions [7, 8]. For example, Cr(III) dominates at acidic to neutral pH and is readily adsorbed or precipitated, while Cr(VI) exists as anionic species (HCrO₄[–], CrO₄^{2–}) that are weakly retained in alkaline soils, although the presence of Ca²⁺ in calcareous soils can enhance Cr(VI) retention and reduce its mobility [9, 10]. Since total elemental analysis provides limited information on environmental risk, single-extraction procedures using chelating agents (e.g., EDTA) or non-chelating salt solutions (e.g., CaCl₂, MgCl₂, NH₄OAc) have been widely developed to estimate the labile or bioavailable metal fraction in soils [11, 12]. More recently, advanced techniques such as diffusive gradients in thin films (DGT) have been used to assess heavy metal bioavailability in water and soil, offering improved predictions of plant uptake [13, 14]. Additionally, the integration of bioavailability-based approaches into regulatory frameworks is increasingly recommended for ecological risk assessment and soil quality standard setting [2, 4, 6]. However, the performance of traditional single extractants has rarely been systematically compared for Cr in arid-zone calcareous soils, such as those extensively found across North Africa, including Libya. Therefore, the present study was conducted on six Libyan agricultural soils (three with high CaCO₃ >30% and three with low CaCO₃ <3%) with the following objectives: (i) to determine Cr bioavailability using eight extractants (0.01 M) at three pH values (4.91, 6.00, 10.14); (ii) to evaluate and compare extractant efficiency; and (iii) to elucidate the effect of pH and carbonate content on Cr transport and retention behavior.

Materials and methods

Soil Sampling and Preparation

Six agricultural soil samples were collected from the Tarhuna district, Libya. Three samples had high calcium carbonate content (>30%, designated group b), and three had low calcium carbonate content (<3%, designated group a). For EDTA extraction only, a larger set of 42 samples was used. All soils were air-dried, crushed, and passed through a 2 mm sieve. Soil compaction and biological activity are known to influence metal mobility and bioavailability, as discussed by [15] and [16], although these factors were not directly measured in the present study.

Physicochemical analysis

Soil pH was measured in a 1:2.5 soil-to-water ratio suspension using a glass electrode [17, 18]. The percentage of organic matter was determined by the Walkley–Black method [19], while calcium carbonate (%) content was measured using the Drouineau volumetric method [20]. Electrical conductivity and temperature were also recorded. Results are presented in (Table 1).

Table 1. Physical and chemical properties of selective soils

samples No	Name of region	Type of area	Deep	PH		CaCO ₃	OM	conductivity	
				Values	temp. °C	%	%	µs	temp. °C
a	Al-Khdra	Olive Cultivated	0 cm	8.5	21.7	0.8	0.774	89	23
b	AlHuwtim	Seeds Cultivated	0 cm	8.7	20.5	1.88	0.891	198	24.2
c	Mingar Al Teer	Olive Cultivated	0 cm	8.8	20.5	1.88	0.032	209	22.6
d	Teryqhlata	Seeds Cultivated	50 cm	9.29	22.6	32.39	0.194	129.1	19.5
e	Suq al Gumaa	Grape Cultivated	50 cm	9.11	22.6	29.42	0.502	127.7	19.5
f	Ash Shuwarif	Seeds Cultivated	50 cm	9.21	20.5	29.42	0.384	295	22.4

Note: OM = organic matter; EC = electrical conductivity; all values represent single measurements per sample.

The assessment of heavy metal bioavailability in soils, including the use of standardized methods and sequential extraction schemes such as the BCR (Community Bureau of Reference) procedure, has been extensively reviewed by [1] and [14]. However, the present study focused on single extractants to provide an operational measure of Cr bioavailability under controlled pH conditions.

Extractants and pH conditions

Eight extractants were prepared at 0.01 M concentration: deionized water (H₂O), EDTA (disodium salt), ammonium acetate (NH₄OAc), ammonium chloride (NH₄Cl), ammonium oxalate ((NH₄)₂C₂O₄), hydroxylamine hydrochloride (NH₂OH·HCl), calcium chloride (CaCl₂), and magnesium chloride (MgCl₂). Each extractant solution was adjusted to three pH values: 4.91, 6.00, and 10.14 using 0.1 M HCl or NaOH without buffering agents to avoid potential complexation with Cr. Final ionic strength varied slightly with pH adjustment but remained within ±15% of the nominal 0.01 M concentration. The pH of each extractant was verified immediately before use; potential pH drift during the 2-hour extraction period was not monitored but is acknowledged as a limitation. The selection of these extractants was informed by previous studies on metal bioavailability in contaminated and agricultural soils [11, 12].

Extraction procedure

Extractions were performed in triplicate for each soil type, extractant, and pH combination. Five grams of air-dried, sieved (<2 mm) soil were mixed with 25 mL of extractant (1:5 soil: solution ratio), shaken for 2 hours, centrifuged at 3,000 × g for 15 minutes, and filtered through 0.45 µm filters. Chromium concentration in the extracts was determined using graphite furnace atomic absorption spectrophotometry (GFAAS). This extraction approach provides an operational measure of potentially bioavailable Cr under controlled pH conditions but does not distinguish between Cr(III) and Cr(VI) species without additional speciation analysis [1, 21].

Total chromium and statistical analysis

Total Cr concentration was determined following aqua regia digestion using HCl: HNO₃, 3:1 v/v. Mean, standard deviation (SD), and range were calculated for each extractant and pH condition. Correlation coefficients (Pearson's r) between EDTA-extractable Cr and organic matter or CaCO₃ were calculated for the 42 soil samples from the Tarhuna district to improve statistical power; these samples included the six soils studied with all extractants. Bioavailability models and statistical approaches for metal risk assessment in soils have been reviewed by [4] and [2], and the methods used here follow standard practices for single-extraction studies.

Results and discussion

Soil properties

The physical and chemical properties of the six selected soils are summarized in (Table 1). Soil pH values ranged from 8.5 to 9.29, indicating strongly alkaline conditions typical of calcareous semi-arid soils. Calcium carbonate contents varied from 0.8% to 32.39%, whereas organic matter contents were generally low (0.032% to 0.891%), and electrical conductivity ranged from 89 to 295 $\mu\text{S}/\text{cm}$. These properties are known to strongly influence heavy-metal retention and mobility in soils [1, 21].

Total chromium concentration

Total Cr concentrations in the studied soils are shown in (Table 2). The mean total Cr was 6.03 mg/kg for low-carbonate soils (group a) and 6.91 mg/kg for high-carbonate soils (group b). These values are within the typical background range for uncontaminated calcareous soils and are similar to those reported in other studies on Cr bioavailability in agricultural systems [5, 14].

Table 2. Total Cr concentrations in the studied soils.

samples No	Total Cr Conc. [mg/kg]	
a Soil samples at depth (0 – 10 cm)	Mean	6.03
	Range	5.25
	SD	1.2336
b Soil samples at deep (40 – 50 cm)	Mean	6.91
	Range	5.6
	SD	1.2535

Chromium extraction at different pH values

To facilitate comparison, extraction results from pH 4.91, 6.00, and 10.14 have been combined into (Table 3) below. Data are presented as mean Cr extracted (mg/kg) and as a percentage of total Cr, separately for low-carbonate (a) and high-carbonate (b) soils.

Table 3. Chromium extracted (mg/kg) and % of total Cr at three pH values using eight extractants (n=3)

Extractant (0.01 M)	Soil Group	pH 4.91	pH 6.00	pH 10.14
Deionized water	a (low CaCO_3)	0.1517 (2.52%)	0.1077 (1.79%)	0.087 (1.44%)
	b (high CaCO_3)	0.200 (2.90%)	0.067 (0.97%)	0.109 (1.58%)
EDTA	a	0.09 (1.49%)	0.188 (3.12%)	0.0956 (1.59%)
	b	0.0723 (1.05%)	0.0836 (1.21%)	0.0116 (0.17%)
Ammonium acetate	a	0.077 (1.28%)	0.046 (0.76%)	0.225 (3.73%)
	b	0.0686 (0.99%)	0.0286 (0.41%)	0.106 (1.53%)
Ammonium chloride	a	0.111 (1.84%)	0.0783 (1.30%)	0.0783 (1.30%)
	b	0.0656 (0.95%)	0.0523 (0.76%)	0.147 (2.13%)
Ammonium oxalate	a	0.093 (1.54%)	0.124 (2.06%)	0.1677 (2.78%)
	b	0.0596 (0.86%)	0.101 (1.46%)	0.081 (1.17%)
Hydroxylamine HCl	a	0.074 (1.23%)	0.11 (1.82%)	0.0653 (1.08%)
	b	0.076 (1.10%)	0.038 (0.55%)	0.053 (0.77%)
Calcium chloride	a	0.0146 (0.24%)	0.112 (1.86%)	0.204 (3.38%)
	b	0.044 (0.64%)	0.1433 (2.07%)	0.059 (0.85%)
Magnesium chloride	a	0.198 (3.28%)	0.091 (1.51%)	0.0184 (0.31%)
	b	0.14 (2.03%)	0.174 (2.52%)	0.156 (2.26%)

Note: Percentages represent Cr extracted relative to total Cr (group a: ~6.03 mg/kg; group b: ~6.91 mg/kg).

Effect of pH on chromium extraction patterns

The results of this study demonstrate that chromium extractability in Libyan calcareous agricultural soils is strongly dependent on the type of extractant, the pH of the extracting solution, and the calcium carbonate content of the soil. As presented in the merged Table 3, the quantities of Cr extracted ranged widely, from a minimum of 0.0116 mg/kg (EDTA, pH 10.14, soil b) to a maximum of 0.225 mg/kg (NH_4OAc , pH 10.14, soil a), which corresponds to 0.17% to 3.73% of total Cr. Although these absolute amounts are small, they fall within or exceed the typical Cr concentration range reported in plants

(0.02–1.5 ppm), indicating potential bioavailability, as discussed by [2, 3]. Furthermore, the shape of the Cr extraction curves differed markedly between high-carbonate (group b) and low-carbonate (group a) soils depending on the extractant type and pH, as illustrated in Figures 1 to 8.

Deionized water

(Figure 1) illustrates the effect of pH on Cr extraction using deionized water. For low-carbonate soils (group a), Cr extraction decreased steadily as pH increased from 4.91 to 10.14, declining from 2.52% to 1.44% of total Cr. In contrast, high-carbonate soils (group b) exhibited a distinct V-shaped pattern, with a minimum extraction of 0.97% at pH 6.00, followed by a slight increase to 1.58% at pH 10.14. This divergence between the two soil groups can be attributed to the retention behavior of Cr(VI) species such as CrO_4^{2-} and HCrO_4^- , which diminishes as pH increases [10, 14]. In alkaline calcareous soils, the presence of Ca^{2+} ions promote Cr(VI) sorption, thereby reducing its mobility [7, 8]. Furthermore, competing anions including HCO_3^- , SO_4^{2-} , and H_4SiO_4 may additionally affect Cr adsorption under field conditions [9, 22].

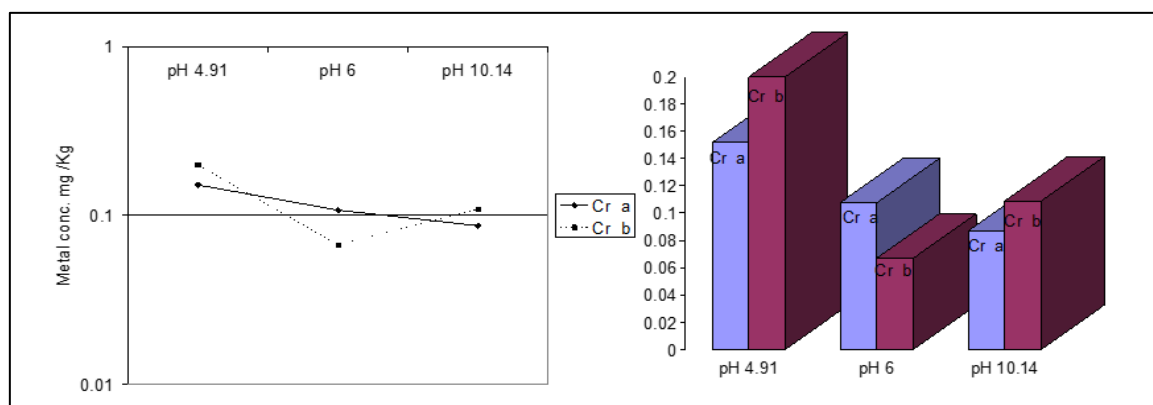


Figure 1. Effect of pH on Cr extraction from Tarhuna soil at a soil:solution ratio of 1:5 using deionized water

EDTA

(Figure 2) presents the extraction pattern obtained with 0.01 M EDTA. Extraction peaked at pH 6.00 for both soil groups, with low-carbonate soils (group a) extracting nearly twice as much Cr (3.12%) as high-carbonate soils (group b, 1.21%). At pH 10.14, Cr extraction from high-carbonate soils dropped sharply to 0.17%, representing the lowest value recorded among all extractants and pH combinations. The relatively poor performance of EDTA, even at its optimal pH of 6.00 (maximum 3.12% for low-carbonate soils), suggests that Cr in these soils is not predominantly bound to organic matter. This finding is consistent with the low organic matter content reported in Table 1 (0.032–0.891%). Similar observations have been documented by [1, 6].

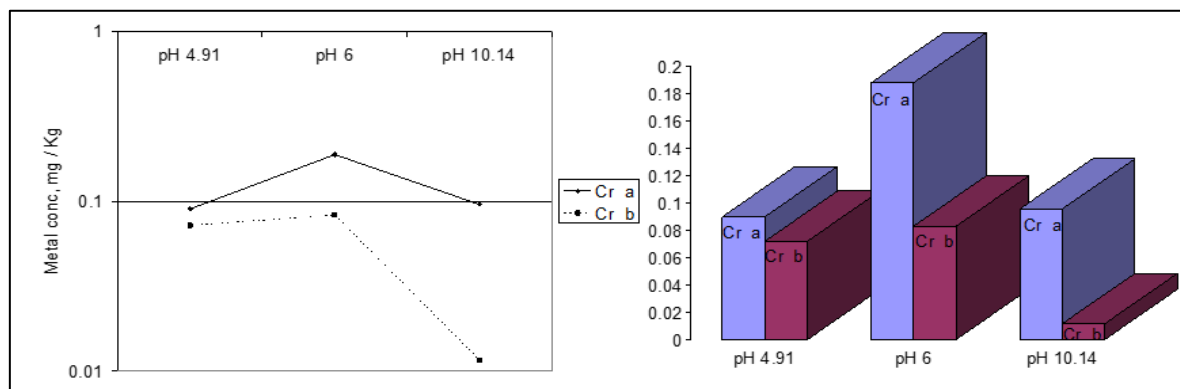


Figure 2. Effect of pH on Cr extraction from Tarhuna soil at a soil:solution ratio of 1:5 using 0.01 M EDTA

Ammonium acetate

(Figure 3) displays the extraction behavior of 0.01 M ammonium acetate. Low-carbonate soils (group a) exhibited a U-shaped curve, with minimum extraction at pH 6.00 (0.76%) and maximum extraction at pH 10.14 (3.73%), which represents the highest overall extraction efficiency recorded in this study. High-carbonate soils (group b) showed a relatively flat response across the pH range, with a slight increase at pH 10.14 (1.53%) and a minimum at pH 6.00 (0.41%). The superior performance of ammonium acetate at pH 10.14 indicates that this alkaline extractant is particularly effective at releasing

Cr(VI) anionic species, which remain soluble and mobile under alkaline conditions [20]. This finding aligns with the observed increase in Cr extraction at high pH for other alkaline extractants such as calcium chloride and magnesium chloride.

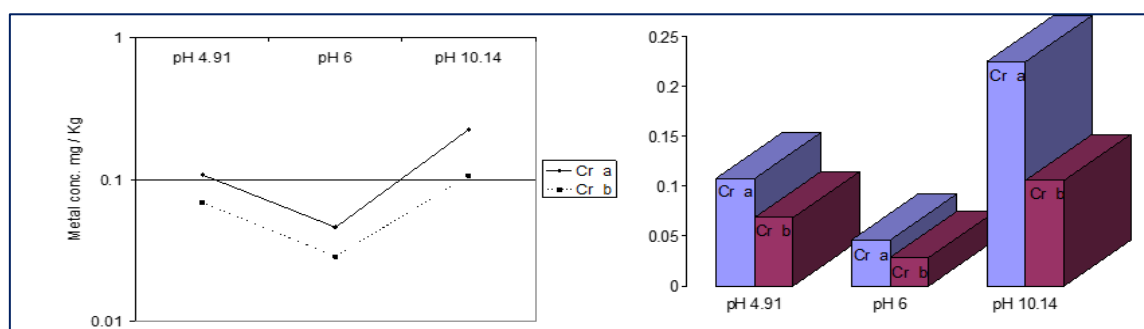


Figure 3. Effect of pH on Cr extraction from Tarhuna soil at a soil:solution ratio of 1:5 using 0.01 M Ammonium acetate

Ammonium chloride

(Figure 4) shows the extraction pattern for 0.01 M ammonium chloride. Both soil groups exhibited increased extraction at pH 10.14, but the increase was more pronounced in high-carbonate soils (group b), which reached 2.13% compared to 1.30% for low-carbonate soils (group a). At pH 4.91, extraction was moderate for both groups (1.84% for group a and 0.95% for group b), while pH 6.00 yielded intermediate values. The enhanced extraction at alkaline pH suggests that ammonium chloride, like other alkaline extractants, is capable of mobilizing Cr(VI) anionic species. The more pronounced response in high-carbonate soils may be related to the displacement of adsorbed Cr(VI) by competing anions or to the dissolution of carbonate surfaces that retain Cr under neutral conditions.

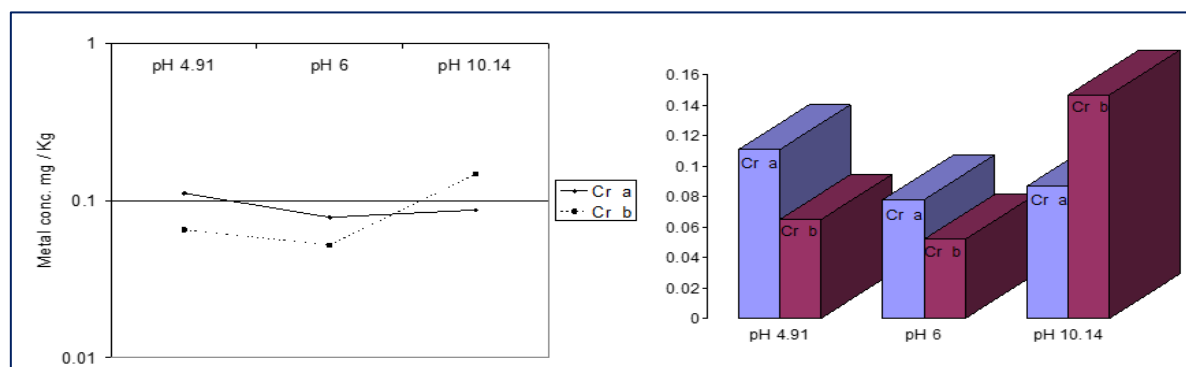


Figure 4. Effect of pH on Cr extraction from Tarhuna soil at a soil:solution ratio of 1:5 using 0.01 M Ammonium Chloride

Ammonium oxalate

(Figure 5) illustrates the extraction behavior of 0.01 M ammonium oxalate. For low-carbonate soils (group a), Cr extraction

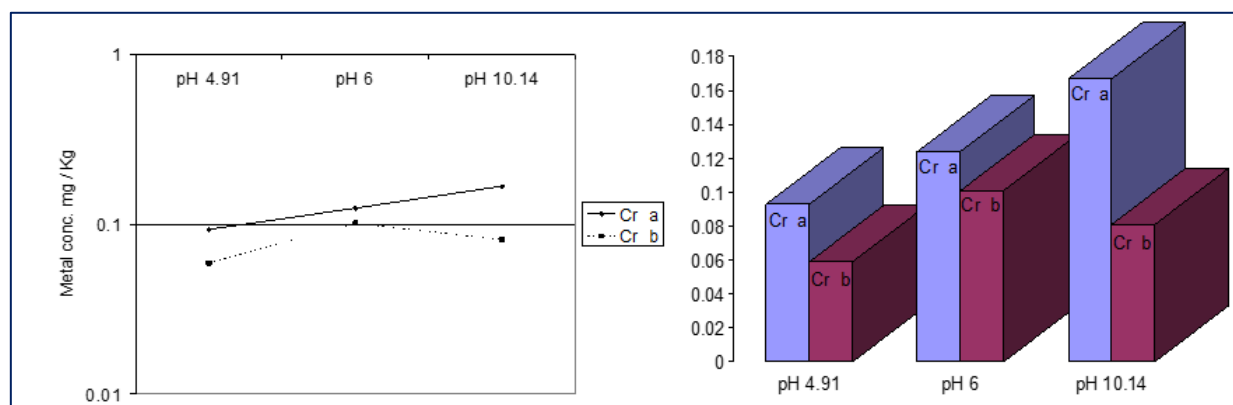


Figure 5. Effect of pH on Cr extraction from Tarhuna soil at a soil:solution ratio of 1:5 using 0.01 M Ammonium Oxalate

increased progressively with rising pH, from 1.54% at pH 4.91 to 2.06% at pH 6.00, reaching a maximum of 2.78% at pH 10.14. In contrast, high-carbonate soils (group b) exhibited a different pattern, with extraction increasing from 0.86% at pH 4.91 to a peak of 1.46% at pH 6.00, before declining to 1.17% at pH 10.14. Among all extractants tested, ammonium oxalate produced the highest extraction in low-carbonate soils at pH 10.14 (2.78%), while its maximum overall performance across both soil groups was observed at pH 6.00 for low-carbonate soils (2.06%). This indicates that ammonium oxalate is particularly effective at releasing Cr associated with iron and manganese oxides through reductive dissolution and complexation, especially under acidic to neutral pH conditions that favor the dissolution of amorphous Fe and Mn oxides and the subsequent release of associated Cr.

Hydroxylamine HCl

(Figure 6) presents the extraction pattern for 0.01 M hydroxylamine hydrochloride. Extraction was low across all pH values for both soil groups. The maximum extraction was observed at pH 6.00 for low-carbonate soils (1.82%), while high-carbonate soils showed their highest extraction at pH 4.91 (1.10%). At pH 10.14, extraction decreased to 1.08% for group a and 0.77% for group b. The generally low extraction efficiency of hydroxylamine HCl across all pH values suggests that this extractant is less effective at mobilizing Cr from these calcareous soils compared to the other extractants tested. This may be related to the specific geochemical forms of Cr present in these soils, which are not readily dissolved by hydroxylamine under the conditions employed.

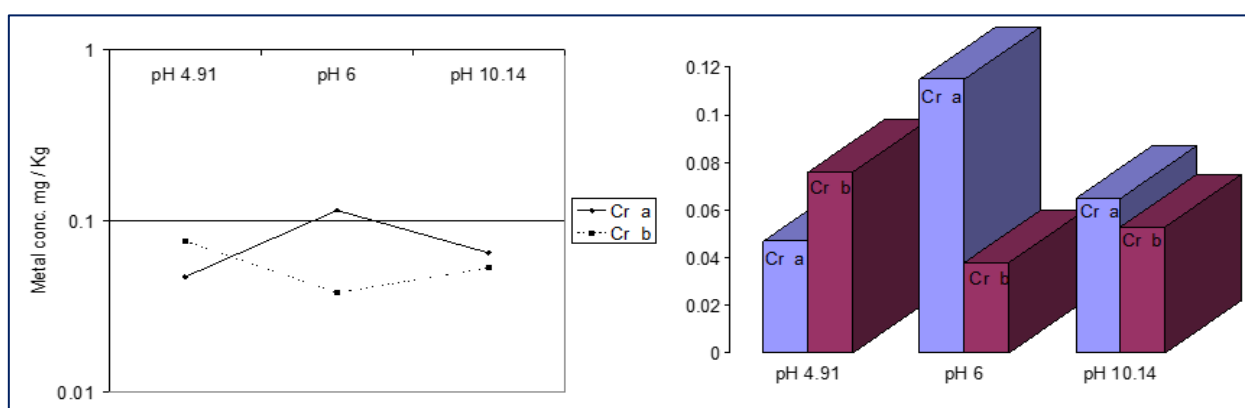


Figure 6. Effect of pH on Cr extraction from Tarhuna soil at a soil:solution ratio of 1:5 using 0.01 M Hydroxylamine Hydrochloride

Calcium chloride

(Figure 7) shows the extraction behavior of 0.01 M calcium chloride. Low-carbonate soils (group a) exhibited a steady increase in Cr extraction with rising pH, from 0.24% at pH 4.91 to 1.86% at pH 6.00 and reaching 3.38% at pH 10.14. High-carbonate soils (group b) showed a different pattern, with maximum extraction at pH 6.00 (2.07%) and lower values at pH 4.91 (0.64%) and pH 10.14 (0.85%). The contrasting patterns between the two soil groups suggest that Cr retention mechanisms differ depending on carbonate content. In low-carbonate soils, the increase in extraction with pH indicates that alkaline conditions favor the mobilization of Cr(VI) anionic species. In high-carbonate soils, the peak at pH 6.00 may reflect the balance between Cr(VI) desorption and re-adsorption onto carbonate surfaces

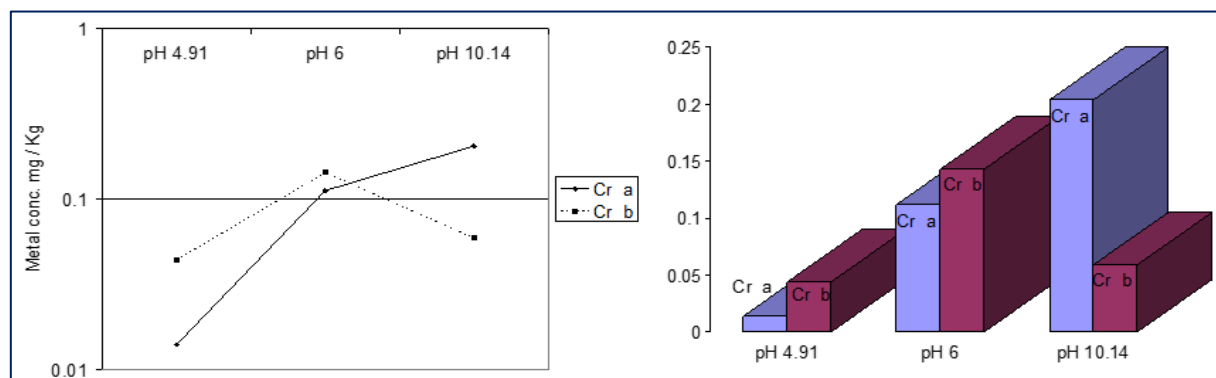


Figure 7. Effect of pH on Cr extraction from Tarhuna soil at a soil:solution ratio of 1:5 using 0.01 M Calcium chloride

Magnesium chloride

(Figure 8) illustrates the extraction pattern obtained with 0.01 M magnesium chloride. Low-carbonate soils (group a) displayed a bimodal pattern, with high extraction at both pH 4.91 (3.28%) and pH 10.14 (0.31%), and a minimum at pH 6.00 (1.51%). High-carbonate soils (group b) showed a progressive increase in extraction with pH, from 2.03% at pH 4.91 to 2.52% at pH 6.00 and 2.26% at pH 10.14. The bimodal pattern observed in low-carbonate soils suggests that different Cr pools are mobilized under acidic and alkaline conditions. At acidic pH, Cr(III) species may be released through proton-promoted dissolution, while at alkaline pH, Cr(VI) anionic species become mobile. The progressive increase in high-carbonate soils indicates that alkaline conditions enhance Cr extraction, likely due to the increased solubility of Cr(VI) and the displacement of adsorbed species by competing anions.

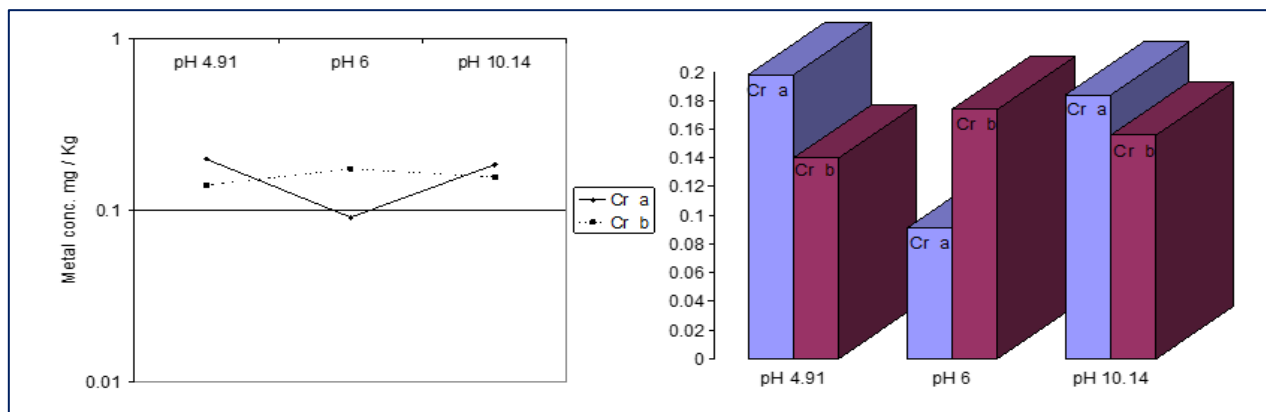


Figure 8. Effect of pH on Cr extraction from Tarhuna soil at a soil:solution ratio of 1:5 using 0.01 M Magnesium Chloride

Correlations with soil properties (n = 42)

For EDTA-extractable Cr and organic matter percentage, correlation coefficients were:

- $r = 0.176$ at pH 4.91
- $r = 0.023$ at pH 6.00
- $r = 0.112$ at pH 10.14

For EDTA-extractable Cr and calcium carbonate percentage:

- $r = -0.038$ at pH 4.91
- $r = -0.208$ at pH 6.00
- $r = -0.266$ at pH 10.14

All correlations were weak and statistically non-significant ($p > 0.05$), indicating that while organic matter and CaCO_3 may influence Cr extractability, they are not dominant controlling factors in these soils. Additional variables such as clay mineralogy, Fe/Mn oxide content, and redox microsites likely contribute to Cr retention and mobility. But these weak positive correlations with organic matter and weak negative correlations with CaCO_3 are consistent with the literature [1, 8, 21].

Conclusions

Comparison of the eight extractants demonstrated substantial variation in chromium extractability as a function of extractant type, pH, and soil carbonate content. Based on the verified Table 3 calculations, the highest extracted fraction was obtained using ammonium acetate at pH 10.14 in low-carbonate soils, yielding 0.225 mg/kg or 3.73% of total Cr. The lowest overall extraction was obtained using EDTA at pH 10.14 in high-carbonate soils, yielding 0.0116 mg/kg or approximately 0.17% of total Cr. Ammonium oxalate showed relatively high extraction under selected conditions but was not the most effective treatment overall. These findings confirm that the operationally extractable Cr fraction depends strongly on extraction chemistry, pH, and soil carbonate status. Because GFAAS measured total Cr in the extracts and no oxidation-state-specific method was applied, the results should not be presented as direct measurements of Cr(VI) or Cr(III). Instead, the pH-dependent patterns are consistent with known chromium speciation chemistry and should be interpreted as mechanistic expectations. Further work using a validated Cr(VI)-specific method and/or sequential extraction would strengthen assessment of chromium mobility and environmental relevance in these calcareous agricultural soils.

References

- Kim RY, Yoon JK, Kim TS, Yang JE, Owens G, et al. Bioavailability of heavy metals in soils: definitions and practical implementation—a critical review. *Environ Geochem Health*. 2015;37:1041–61. doi: 10.1007/s10653-015-9695-y.
- Peijnenburg WJGM. Implementation of bioavailability in prospective and retrospective risk assessment of chemicals in soils and sediments. In: Ortega-Calvo JJ, Parsons JR, editors. *Bioavailability of Organic Chemicals in Soil and Sediment*. Vol. 100. Cham: Springer; 2020. p. 391–422. doi: 10.1007/978-90-481-9757-6.
- Hodson ME, Vijver MG, Peijnenburg WJGM. Bioavailability in soils. In: Swartjes F, editor. *Dealing with Contaminated Sites*. Dordrecht: Springer; 2011. p. 721–46. doi: 10.1007/978-90-481-9757-6.
- Mebane CA, Chowdhury MJ, De Schampheleere KAC, Lofts S, Paquin PR, et al. Metal bioavailability models: current status, lessons learned, considerations for regulatory use, and the path forward. *Environ Toxicol Chem*. 2020;39:60–84. doi: 10.1002/etc.4560.
- Shahid M, Dumat C, Khalid S, Schreck E, Xiong T, Niazi NK. Foliar heavy metal uptake, toxicity and detoxification in plants: A comparison of foliar and root metal uptake. *Chemosphere*. 2017;178:513–33. doi: 10.1016/j.chemosphere.2017.03.066.
- Oorts K, Smolders E, Lanno R, Chowdhury MJ, et al. Bioavailability and ecotoxicity of lead in soil: implications for setting ecological soil quality standards. *Environ Toxicol Chem*. 2021;40:1948–61. doi: 10.1002/etc.5051.
- Avudainayagam S, Naidu R, Kookana RS, Alston AM, McClure S, Smith LH. Chemistry of chromium in soils with emphasis on tannery waste sites. *Aust J Soil Res*. 2001;39:1077–89. doi: 10.1071/SR00023.
- Echeverría J, Morera T, Garrido J. Retention of heavy metals by soils and components. *Aust J Soil Res*. 1999;37:431–41. doi: 10.1071/SR98105.
- Bartlett RJ, Kimble JM. Behavior of chromium in soils: II. Hexavalent forms. *J Environ Qual*. 1976;5:383–6. doi: 10.2134/jeq1976.00472425000500040010x.
- Wittbrodt PR, Palmer CD. Effect of temperature, ionic strength, background electrolytes, and pH on the reduction of hexavalent chromium by soil humic substances. *Environ Sci Technol*. 1995;29:255–63. doi: 10.1021/es00001a032.
- Gupta SK, Aten C. Comparison and evaluation of extraction media for the determination of trace metals in soils. *J Environ Anal Chem*. 1993;51:25–40. Ure AM. Single extraction schemes for soil analysis and related applications. *Mikrochim Acta*. 1991;11:49–57.
- Zhu Q, Ji J, Tang X, Wang C, Sun H. Bioavailability assessment of heavy metals and organic pollutants in water and soil using DGT: a review. *Appl Sci*. 2023;13:9760. doi: 10.3390/app13179760.
- Chen R, Yang J, Cai X, Liu Z, Huang W, et al. Assessing soil remediation effect of Cr and Pb based on bioavailability using DGT, BCR and standardized determination method. *Sci Total Environ*. 2024;953:175947. doi: 10.1016/j.scitotenv.2024.175947.
- Beylich A, Oberholzer HR, Schrader S, Höper H, Wilke BM. Evaluation of soil compaction effects on soil biota and soil biological processes in soils. *Soil Tillage Res*. 2010;109:133–43. doi: 10.1016/j.still.2010.05.010.
- Padoan E, Kath AH, Vahl LC, Ajmone-Marsan F. Potential release of zinc and cadmium from mine-affected soils under flooding, a mesocosm study. *Arch Environ Contam Toxicol*. 2020;79:421–34. doi: 10.1007/s00244-020-00777-0.
- McKeague JA, editor. *Manual on soil sampling and methods of analysis*. 2nd ed. Ottawa: Canadian Society of Soil Science; 1978.
- McLean FO. Soil pH and lime requirement. In: Page AL, Miller RH, Keeney DR, editors. *Methods of Soil Analysis*. Part 2. Chemical and Microbiological Properties. 2nd ed. Madison: ASA; 1982. p. 199–224.
- Jackson ML. *Análisis químico de suelos*. 3rd ed. Barcelona: Ediciones Omega; 1982.
- Drouineau G. Dosage rapide du calcaire actif du sol. *Ann Agron*. 1942;12:411–50.
- Guan D, Ji X, Liu S, Chen S, Xie Y, et al. Exploration of the bio-availability and the risk thresholds of cadmium and arsenic in contaminated paddy soils. *Heliyon*. 2024;10:e40910. doi: 10.1016/j.heliyon.2024.e40910.
- Zachara JM, Cowan CE, Schmidt RL, Ainsworth CC. Chromate adsorption on soil minerals. *Environ Sci Technol*. 1987;21:589–94. doi: 10.1021/es00160a006.
- McLean JE, Bledsoe BE. *Behavior of metals in soils*. Washington, DC: U.S. Environmental Protection Agency; 1992. EPA Ground Water Issue. EPA/540/S-92/018.