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Study of copper adsorption in some calcareous soils and calcium carbonate in North of Iraq

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Abstract

This study aimed to investigate the ability of calcium carbonate mineral (Calcite) and calcareous soils as an adsorbent to remove heavy metals (Cu) in aqueous media by using the mechanism of adsorption phenomena. Isotherm adsorption was conducted using the Batch technique, using different Cu concentrations of (0, 5, 10, 50 and 100) $\mu\text{g Cu.ml}^{-1}$ for 24 hours. at 298K. The results showed that copper adsorption on the Calcite mineral surface was 2019 mg.kg^{-1} while the number of Cu-removals in calcareous soils increased as soil carbonate minerals content increased and ranged between (2035-2487) mg.kg^{-1} . The magnitude of calcium carbonate on Cu adsorption as active masterly in the adsorption. R^2 (0.87) K_d for soils (230-7556) were than carbonate minerals (258) L Kg^{-1} also Langmuir parameters values adsorption for calcareous soils were more than calcium carbonate mineral (Calcite) respectively, (X_m), (1429, 4526) mg kg^{-1} , L (0.125 120.5) L mg^{-1} , MBC , 178.63 2590.3) Kg^{-1} and RL 0.102 0.779, for mineral (Calcite) and calcareous soils respectively and the adsorption process was spontaneous.

Keywords: Calcium carbonate, adsorption capacity, industrial effluents

1. Introduction

Copper pollution is considered one of the major problems in the world as it contributes significantly to the pollution of the agricultural system (soil and water) and pollutes industrial and human activities, from additives to fungicides and factory wastes such as sheet metal and paint, fertilizer, mining operations, and texture factories Organic and inorganic compounds have a role in increasing copper deposition and forming low-soluble complexes (Ahmad *et al.*, 2012) ^[28]. All heavy metals are toxic and non-biodegradable, these metals exist in wastewater and natural water. Among these compounds, the most dangerous and detrimental are the heavy metals, which can accumulate within living tissues, even in low quantities. (Ahmad *et al.*, 2012) ^[28]. Various techniques are employed to remove heavy metals, including ion exchange, chemical deposition, membrane separation, liquid extraction, electrodialysis, and adsorption (Al-Hayani *et al.*, 2022) ^[29]. Using powders such as activated carbon, silica, alumina, etc., Effectively eliminates heavy elements. However, the manufacturing process of these powders generates environmental pollutants. Consequently, there is a shift towards employing alternative materials (Natural powders) that are abundant, unused, or found in waste sources (Al-Hassoon *et al.*, 2019) ^[2]. Consequently, many studies have been conducted on different categories of natural substances that have demonstrated efficacy in removing heavy metals, such as Bentonite and Silicate clay minerals (Akrawi *et al.*, 2021) ^[1]. Calcium carbonate with several organic substances the lime and calcium carbonate were utilized to remediate groundwater contaminated with heavy metals from an abandoned mine (Alghamdi & Alasmay, 2023) ^[30]. Calcareous soils contain high calcium carbonate therefore regarded a good and very cheap adsorptive materials. (Allison & Allison, 2005) ^[4]. They can extract heavy metals from aqueous solutions, a method used to treat water and solutions contaminated with copper. Additionally, they can be used to determine the adsorbed ion's maximum adsorption capacity and binding capacity (Al-Tamimi, 2004; Nawfal & Ali, 2018) ^[3, 31]. Used calcareous soil and calcium carbonate mineral as a good and very cheap adsorptive materials for water and waste water treatment and indeed they are

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widely used due to their higher output and low cost (Alloway, 2013) ^[6]. It has been found that lime rock samples containing impurities such as silica, iron, aluminum oxides, and various clay minerals exhibit an improved ability to absorb substances. The environmental consequences of introducing metal into soil or minerals are contingent upon their sorption capacity. Adsorption is a crucial chemical reaction in soils. It enhances the ability of soil to release metals from its surfaces, making it one of the main processes responsible for the transportation of metals and contaminants in soils (Alloway). The soil's ability to retain the sorbet and the energy that binds it to the soil (Babel & Kurniawan, 2003) ^[7]. The factors that influence soil pH include the ionic strength and content of the solution. Furthermore, the increase in soil pH directly impacts Cu sorption. This is because the rise in pH increases the overall number of negatively charged sites on clay minerals and Organic Matter (OM), enhancing the soil's ability to sorb Cu. It is essential to enhance the individual sorption characteristics to effectively address the environmental hazard presented by Cu and its availability (Lammers *et al.*, 2017) ^[16]. The adsorption and precipitation processes occurring on the surfaces of soil solids result in a reduction of the concentration of Cu in the solution phase. Copper has greater solubility in acid soil compared to calcareous soils individually. Many isotherm models are used to describe adsorption phenomena as Langmuir, Freundlich's Timken DR equations (Alloway, 2013) ^[6]. Our research was carried out to use calcareous soil and calcium carbonate minerals as good and very cheap adsorptive materials. To remediate copper from water and wastewater by using batch method.

2. Materials and Methods

2.1. Sample size

Soil samples were collected from Ninavha province of northern Iraq, according to different CaCO₃ clay and soil organic matter contents from the soil rhizosphere layer (0-0,30) m, and analyzed for several properties, including CaCO₃ clay and soil organic matter concentration. The soil samples underwent a process of drying, crushing, and filtration through a sieve with a 2-mm mesh size. The chemical and physical characteristics of the soil were then analyzed using the methods provided by (Das *et al.*, 2013; Hooda, 2010) ^[9, 11]. The hydrometer method is used to carry out Soil Separators. The Electrical Conductivity (EC) and soil pH are also determined using a 1:2.5 soil-to-water suspension. Organic matter is calculated using dichromate oxidation, while Calcium Carbonate minerals are assessed using a calorimeter. The isotherm adsorption experiment was conducted using the batch equilibrium method described in reference (Hooda, 2010) ^[11]. A (2) g sub-sample of soil was taken from each sample and mixed with 50 ml of CuCl₂ solution at varied concentrations of Cu (0, 5, 10, 50, 100) mg.l⁻¹ Cu. The soil suspensions were agitated for 30 minutes and allowed to stabilize for 24 hours at a temperature of 298K ±1. The concentration of copper in the clear extract solution was measured using an Atomic Absorption Spectrophotometer (AAS). The amount of copper sorbed by soils was calculated by subtracting the

initial copper concentration from the equilibrium solution's final concentration. The amount of adsorption of Cu was calculated according to the following equation:

$$\text{Cu-ads} = (C_i - C_f) \times V/m \quad (1)$$

Whereas: M -ad. = ion of (Cu²⁺) adsorbed in units (mg kg⁻¹), C_i=ion concentration before Equilibrium (mg L⁻¹), C_f = concentration of ion after equilibrium (mg L⁻¹), volume of added solution (ml), and m=soil mass (g).

According to (Hong *et al.*, 2011) K_d values can be obtained from the use of the Batch technique using the following relationship:

$$K_d = S / C \quad (2)$$

Whereas: S = The amount of ion adsorbed in unit (mg kg⁻¹), C= concentration of the ion in the solution with (mg L⁻¹), and the distribution coefficient unit (K_d) expressed as (L kg⁻¹) Langmuir (1913) model (Lammers *et al.*, 2017) ^[16]:

$$\text{Langmuir: } C/(X/m) = 1/KS_m + 1/S_m \quad (3)$$

RL was derived using the following equation:

$$RL = (1+KL)C_0 \quad (4)$$

3. Results

3.1 General characterizes

Table 1 shows the measured properties of soil samples categorized as Aridisols (Specifically, calcareous soil). These soils' soil response pH values ranged from 7.27 to 8.0, indicating that the examined soil is alkaline. The soil's carbonate mineral concentration ranged from 250 to 375 g kg⁻¹ gm, confirming the presence of calcareous soils. The elevated pH levels and abundance of carbonate minerals in the analyzed soil samples are mainly attributed to the arid climate and nearby carbonate rocks. The elevated pH level will result in the adsorption of metals onto the particles of organic matter by generating negative charges on the humic substances, which are components of organic matter. This method will facilitate the movement of heavy metals in the environment. Calcium carbonate particles frequently create potent sorption sites for heavy metals like copper, making them inaccessible to plants (Allison & Allison, 2005) ^[4]. This serves as a buffer, regulating soil pH at a high alkaline level. The organic matter (SOM %) in the examined soils exhibited flocculation ranging from 7.0 to -24.0 gm kg⁻¹ (Table 1). In general, the soils in Iraq have a low concentration of organic matter since there is very little addition of crop wastes and manure, the land is very dry, and tillage operations are only done during certain seasons. However, it plays a crucial role in the adsorption and absorption of metals in soil. The clay content ranged from 278 to 525 Kg⁻¹ SOM (soil organic matter) and clay contents enhance the interaction between inorganic contaminants and soil (Table1).

Table 1: Physicochemical characteristics of the soil

No.	Location	pH	EC	SOM	CaCO ₃	Particle size distribution		
						Sand	Silt	Clay
			$\mu\text{S/cm}$			g. kg^{-1}		
1.	Al-Kuba	7.70	364	17	375	199	276	525
2.	Humedat	7.71	369	24	369	201	279	520
3.	Al-Abasyia	7.89	383	16	370	193	290	517
4.	Telkeef	7.77	344	16	380	210	280	510
5.	Bsatlyia	8.00	399	17	365	223	272	505
6.	Filfeel	7.75	530	16	360	125	385	490
7.	Uklaa	7.68	367	18	320	275	360	365
8.	Al Khudhir	7.27	2600	23	275	217	458	325
9.	Shoora	7.75	1982	7	250	468	252	278

3.2 Effect of initial concentration on copper removal

Initially, the adsorption of Cu^{++} showed a quick increase with the concentration of the solution, and the adsorption rate approached 100%. Furthermore, the adsorption amounts of Cu in all soil and calcium carbonate powder samples were nearly identical. This phenomenon can be explained by numerous adsorption sites on the soil surface, particularly when the solution concentration is low, and the adsorption rate is high. This is because the adsorption capacity has yet to reach its saturation point. The predominant processes in this stage were nonspecific adsorption and physical adsorption. Subsequently, the Cu^{++} ions gradually filled the adsorption sites, decelerating the rate at which the adsorption amount increased. As a result, the adsorption-isotherm curve exhibited a moderate slope and eventually reached a state of adsorption equilibrium. This process may occur due to particular and chemical adsorption (Al-Hassoon *et al.*, 2019) [2]. An investigation was conducted to examine the adsorption of Cu(II) ions from an aqueous solution onto the solid phase of soil at an initial temperature of 298 K. Tables 2 and 3 display the corresponding outcomes based on the initial concentration of Cu(II)(Co) , the equilibrium concentration (C_e), and the amount of adsorption on the soil matrix (Q_e). The findings demonstrated a rise in the adsorptive ability of nine soils as the concentration of Cu (II) escalated, eventually reaching a maximum value. The heterogeneity of the soil surface is due to the varying properties of unsaturated adsorption sites, resulting in variable energy characteristics of these sites (Lammers *et al.*, 2017) [16]. The existence of surface imperfections and pollutants can significantly impact the situation. The adsorption occurs due to various forces, resulting in the arrangement of adsorbed molecules on the surface in the shape of cultures or spaced lines (Alloway; Babel & Kurniawan, 2003) [6]. Results revealed that CaCO_3

and calcareous soils significantly adsorbed copper from aqueous solution, and the concentration of Cu^{+2} is shown in Tables (2 and 3) before and after equilibrium of more than 80% in CaCO_3 and 90% in studied soils (Hong *et al.*, 2011) [10]. Our finding showed that calcareous soils are good for removing heavy metal ions, making them a viable and efficient substitute for removing metals from actual industrial wastewater.

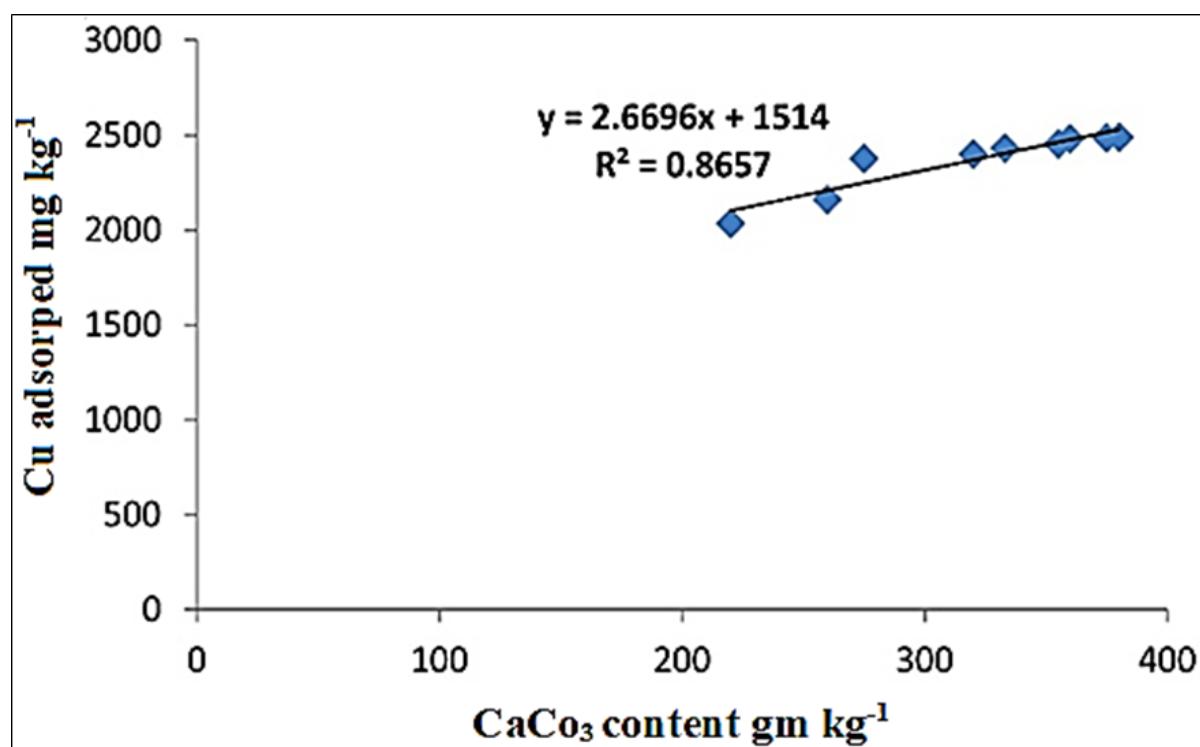
Certain adsorption isotherms are a fusion of chemical and physical adsorption curves. Also Fig. (2) Shows that Cu^{+2} sorption in studied soils is arranged according to Adsorption capacity (x/m) (mg. Kg^{-1}). Fig. (3) Shows that the rate of Cu^{+2} sorption during (step A) in diffusion-controlled (step B) was operationally defined as the Cu^{+2} sorption in the first fifteen minutes of the reaction. This step is probably due to the adsorption of Cu^{+2} at easily accessible sites on the hydrated layer. This is supported by the fact that the addition of various concentrations of Cu^{+2} leaves the solution under-saturated with respect to the Cu^{+2} solid phases in the first reaction periods (in a 1-hour reaction time), but for the longer reaction periods ≥ 20 hours (Rashad *et al.*, 2005) [21]. In the discussion below, it is shown that the Cu^{+2} sorption statistics align with the following explanation. (Step A) - The process of adsorption of Cu^{+2} onto the surface of calcite (Step B) - The process of Cu^{+2} spreading into the outer layer of hydrated calcium carbonate. Step C The production of a solid solution consisting of copper, hydroxide, and carbonate occurs with the growth of new crystalline material from hydrated calcium carbonates, such as $\text{Cu}_x(\text{CO}_3)_x(\text{OH})_x$. The adsorption of Cu^{+2} on the calcite surface may occur by exchanging with deposited Ca^{+2} rather than the release of protons, which is typically observed for hydroxide. (Mehmedany *et al.*, 2016; Rashad *et al.*, 2005; Titi & Bello, 2015) [20, 21, 27].

Table 2: Effect of initial copper addition on Cu removal (%) and Adsorption capacity on calcium carbonate powder

pH	C initial	C final	Cu removal (%)	Adsorption capacity (x/m)(mg.Kg ⁻¹)
	mg.l ⁻¹			
6.48	5	0.6	88.00	110
7.45	10	1.04	89.60	224
7.51	50	2.27	95.46	1193
7.42	100	19.24	80.76	2019

Table 3: Effect of initial copper addition on Cu removal (%) and adsorption capacity in studied calcareous soils

Soil No.	pH	C initial	C final	Cu removal (%)	Adsorption capacity (x/m) (mg.Kg ⁻¹)
		mg.l ⁻¹			
1.	7.37	5	0.40	92.0	115
	7.39	10	0.68	93.2	233
	7.23	50	2.13	95.7	1196
	7.00	100	4.90	95.1	2377
2.	7.73	5	0.02	99.6	124
	7.68	10	0.06	99.4	248
	7.45	50	0.10	99.8	1247
	7.40	100	0.50	99.5	2487
3.	7.72	5	0.36	92.8	116
	7.73	10	0.80	92.0	230
	7.49	50	2.72	94.6	1182
	7.18	100	4.08	95.9	2398
4.	7.47	5	0.10	98.0	122
	7.53	10	0.22	97.8	244
	7.49	50	0.83	98.3	1229
	7.45	100	1.72	98.2	2455
5.	7.44	5	0.45	90.0	112
	7.47	10	0.90	91.0	227
	7.34	50	1.36	96.8	1210
	7.19	100	2.72	97.3	2432
6.	7.56	5	0.27	94.6	118
	7.55	10	1.36	86.4	216
	7.42	50	4.08	91.8	1148
	6.52	100	13.62	86.4	2159
7.	7.60	5	0.04	99.2	124
	7.30	10	0.08	99.2	248
	7.18	50	0.21	99.6	1244
	7.15	100	0.64	99.4	2484
8.	7.19	5	0.01	99.8	124
	7.22	10	0.02	99.8	249
	7.24	50	0.64	98.7	1234
	7.31	100	0.72	99.3	2482
9.	7.11	5	0.42	91.6	114
	7.17	10	0.80	92.0	230
	7.05	50	4.50	91.0	1137
	6.67	100	18.6	81.4	2035

**Fig 1:** Effect of total CaCO₃ on Cu adsorption in study soils

3.3 Copper distribution coefficient

The relationship between the concentration of the adsorbed agent on the soil surfaces and its concentration in the soil solution is called Kd (Partition distribution coefficient) (Soares & Alleoni, 2006) [23]. The coefficient in question represents the soil's capacity to retain the element and is connected to the element's mobility within the soil solution. The values of the Cu^{+2} diffusion coefficient (Kd) between the soil solution and its solid phase are presented in Table (4). The adsorption of copper (II) on the examined soils exhibited the following Kd values: 4139, 4001, 7556, 1309, 259, 408, 460, 571, 230, and 258 L.Kg^{-1} for soil numbers 2, 4, 8, 5.6, 3, 1, 7, and 9, respectively. Calcium carbonate was present in the soils. Estimating Kd as a linear modulus is not feasible due to the intricate nature of soil components and the competition among various metals. Adsorption or soil retention of heavy metals typically occurs at low concentrations, further complicating the estimation. The number 24 is enclosed in square brackets (Bashir *et al.*, 2019) [8]. The study revealed that the distribution coefficient values for Cu^{+2} ranged from 9.4 to 217.1 $\text{cm}^3 \text{g}^{-1}$ and were

influenced by the initial concentration of the solution. The relationship between the distribution coefficient and the initial concentration of the metal was found to be inversely proportional, indicating that as the initial concentration of the metal increased, the distribution coefficient decreased. This relationship is attributed to changes in the properties of the adsorption sites. The elevated Kd values are associated with the strong affinity of the sites for adsorbing heavy metals with high bonding capacity. However, the adsorption sites become saturated at high concentrations, leading to a fall in Kd and a loss of selectivity (Song *et al.*, 2005) [24]. The variation in the Cu^{+2} affinity of the soil constituents can be attributed to factors such as the hydrolysis constant of pH, electrolysis, acidity, charge density, and solubility (Ksp) of sediments. The elevated Kd values indicate the significant influence of mineral and organic colloids in soils, particularly crystallized and non-crystallized iron oxides and carbonate minerals. These substances can lead to the adsorption and precipitation of metals onto these colloids (Hong *et al.*, 2011; Sparks, 2017) [10, 25].

Table 4: Mean values of diffusion or distribution coefficient (Kd)

Location	Kd (L.Kg^{-1})
CaCO_3	258
Humedat	4139
Talkeef	4001
Al-Khudhir	7556
Bsatilyia	1309
Filfeel	259
Al-Abasyia	408
Al-Kuba	460
Uklaa	571
Shoora	230

3.4 Langmuir adsorption isotherms of soils. adsorption isotherms curves

To effectively assess the environmental impact of copper and its availability, it is essential to examine the individual sorption characteristics of copper. The Langmuir equation was used to analyze the sorption data and forecast how copper sorption occurs in different soils (as shown in Table 5). The Langmuir equations, regardless of the amount of copper supplied, exhibited higher accuracy (R²). These findings align with previous studies (Kim *et al.*, 2012; Rashad *et al.*, 2005; Song *et al.*, 2005) [15, 21, 24] conducted on calcareous soils. The adsorption isotherm's configuration can be utilized to determine the adsorption mechanism and the characteristics of adsorption. Adsorption from a solution is believed to be a constant function of the solution's concentration. Copper adsorption isotherms are shown in Figure (4 a,b). The shape of the Cu-adsorption curve on soil is consistent with the L-shape –type according to the Giles classification.

The isotherm of the described system followed the Langmuir equation, indicating a strong adsorption affinity between copper II and the clay surface. Additionally, it suggested the creation of a single adsorption layer of copper II on the soil surface. Giles' interpretation of the adsorption isotherm suggests that the copper might be aligned parallel to the clay surface, alternatively, an abundance of negative charge (Shaheen *et al.*, 2013) [22]. The surplus of negative

layer charge is balanced externally by the adsorption of big ions on the surfaces of the layer, as they cannot fit within the crystal's interior. Within a water-based solution, the cations that balance the charge on the surfaces of the layers can readily be replaced by other cations in the solution. Gouy-Chapman's theory allows for the prediction of clay behaviour in solution based on the concept of the diffuse double layer (Alloway, 2013) [6]. Consequently, the clay particles in a water solution carry an electric charge. The Langmuir constants (b) and (k) for Cu retention in calcareous soils are provided in Table 4. (1) Coordination complex formed by ligands directly bonded to the central metal ion. The term "outer-sphere complex" refers to the interaction between ions or molecules in a solution where the solvent molecules are directly involved in the reaction. The ions disperse and heat up. Formation of hydroxyl complexes occurs. The topic is the affinity of ions for creating organic mineral complexes and their stability. 6-interaction with non-crystalline hydroxides. The outer sphere will add to nonspecific sorption.

The third category of sorption occurs when hydrated ions are drawn to the surface due to electrostatic forces generated by charged surfaces. The soil texture plays a crucial role in retaining and releasing trace elements. Soils with a coarse texture have a lesser propensity for sorbing trace elements than soils with a fine texture (Karim, 2020; Karim, 2018; Lü *et al.*, 2017) [13, 14, 19].

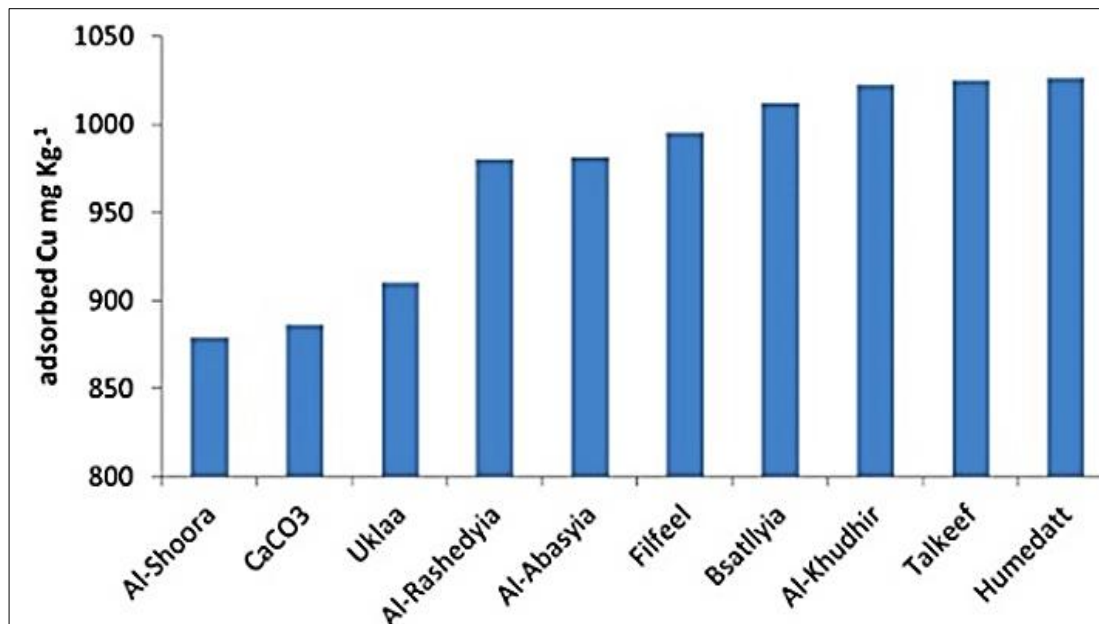


Fig 2: Soil Arrangement according Adsorption capacity (x/m) (mg.Kg⁻¹) in study soils

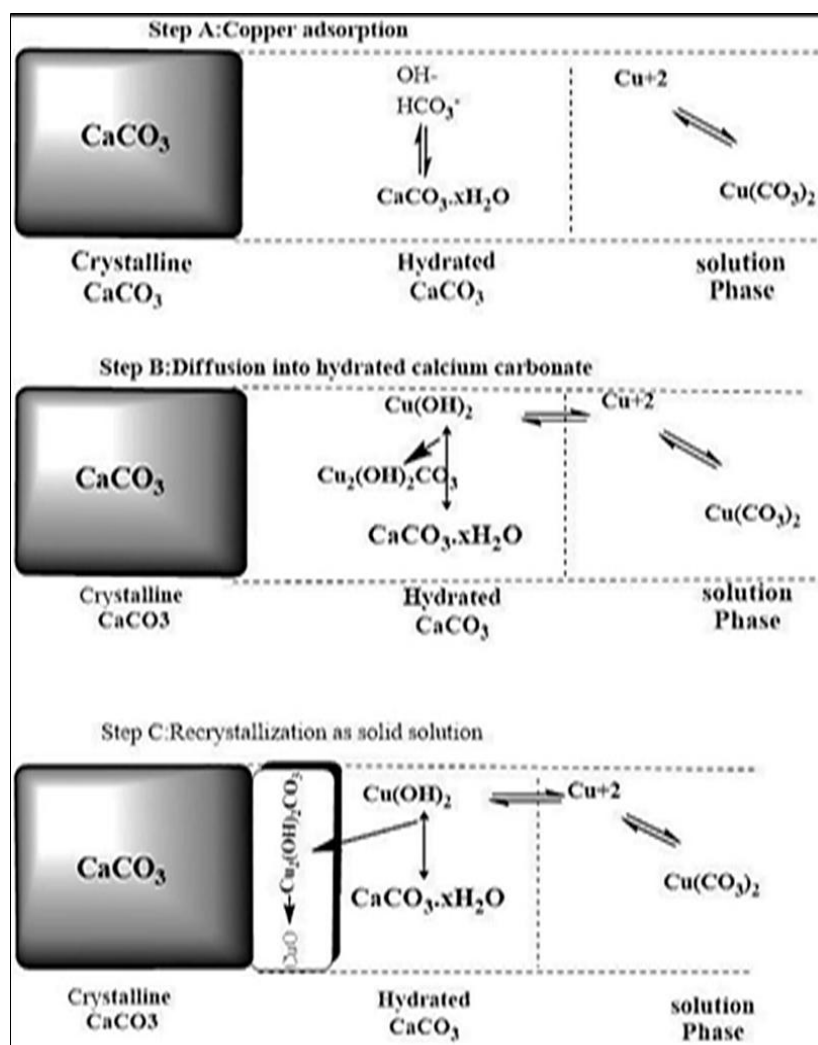
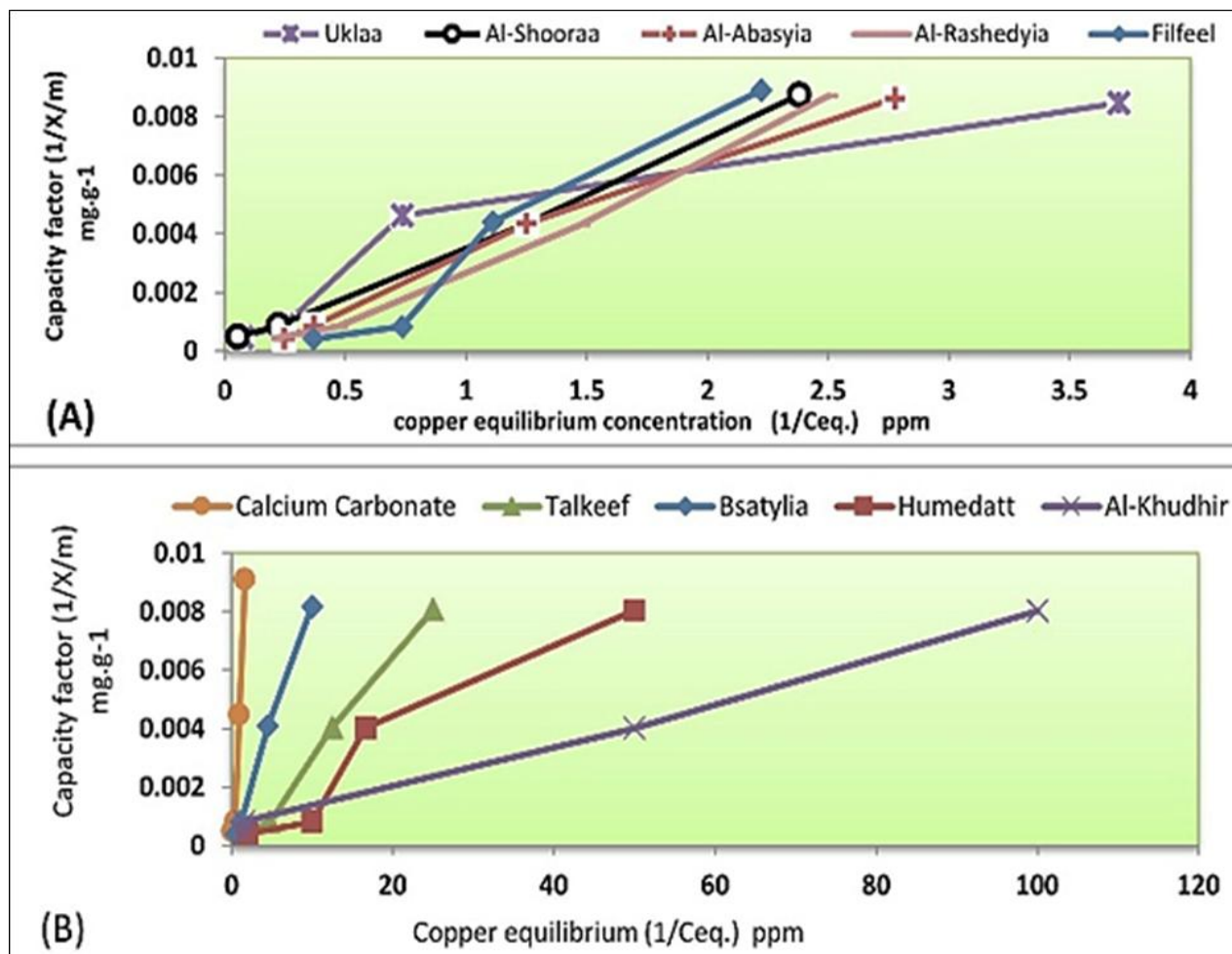


Fig 3: Model for Cu²⁺ sorption processes at calcite-water interface

Table 5: Langmuir adsorption isotherms parameters

Soil name (#)	Langmuir equation	R ²	X _m	K _L	MBC	R _L
CaCO ₃	Y=0.0056x-0.0007	0.96	1429	0.125	178.63	0.102
AlKiba	Y=0.0037 x-0.0007	0.99	1429	0.189	270.35	0.119
Humedatt	Y=0.0002 x-0.0001	0.94	10000	0.500	5000	3.922
Al-Abasyia	Y=0.0036 x-0.0001	0.99	278	0.028	7.72	0.199
Bsatlyia	Y=0.0008x-0.00005	0.99	20000	0.063	1250	0.596
Filfeel	Y=0.0048 x-0.0017	0.96	588	0.354	208	0.218
Uklaa	Y=0.0021 x-0.0012	0.87	833	0.571	476	0.070
Talkeef	Y=0.0003 x-0.0004	0.99	2500	1.333	3333	1.786
Al-Khudhir	Y=0.00008x-0.0094	0.99	106	117.50	12455	0.010
Al-Shooraa	Y=0.0032x-0.0002	0.99	5000	0.063	312.5	0.091

**Fig 4 A, B:** The correlation between copper equilibrium concentration and capacity factor for calcareous soils and calcium carbonate

3.5 The bonding energy

The bonding energy is a reliable indicator of the interaction between the introduced ion and the adsorption surface. The values for Langmuir parameter bonding energy (K_L) Results in Table (5) showed that the affinity of Cu^{+2} bonding (K_L) varied with soil types and ion species concentration, high value was recorded in Humedate soil (117.5 high CaCO_3 content, while the lowest value was recorded 0.028) low CaCO_3 content comparing with CaCO_3 powder (0.125), The magnitude of a chemical reaction's spontaneity and the resulting stability are directly proportional. This phenomenon can be elucidated by two mechanisms: ionic deposition in the form of carbonate and the substitution of the additional ion for calcium in carbonate, as well as the adsorption of ions on the surface of carbonate. The ability of carbonate minerals to adsorb Cu^{+2} ions is attributed to the electrical charge present on the

surfaces of carbon metal. This charge arises from the rearrangement of the calcite metal surfaces, which leads to the influx of relatively small positive ions into the crystal and the outward movement of large negative carbonate ions, resulting in a negative charge. The exterior of a little calcium carbonate crystal the affinity coefficient (K_L) provides a comparative measure of the ease with which the additional Cu^{+2} ions are adsorbed onto or released from the adsorbing surface. According to references (Hooda, 2010) [11], smaller K_L values suggest that a larger quantity of adsorbed Cu^{+2} would be transformed to a non-exchangeable state by producing crystalline Cu^{+2} or through occlusion. K_L is a measure of the adsorbate's affinity for the adsorbent. The bonding energy (K_L) for the surface layer of Cu^{+2} was measured to be 0.01 L mg⁻¹ at a temperature of 298 Kelvin. The researchers noted that high values of K_L indicate a strong attraction between sorbed Cu^{+2} and the soil surface,

which serves as the sorbent surface in the study of sorption (Akrawi *et al.*, 2021) ^[1]. The factors that influence soil pH include the ionic strength and content of the solution.

Furthermore, it should be noted that alterations in soil pH have a direct impact on sorption. Specifically, an increase in soil pH increases the overall number of negative sites present in clay minerals and Organic Matter (OM). Consequently, this increase in negative sites enhances the sorption capacity. It is worth mentioning that a high KL value serves as an indicator of a substantial clay content within the soil. Additionally, it provides insight into the strength of the bonding between clay minerals and other components within the soil.

Additionally, it was discovered in an identical vicinity. The clay concentration in the soil possesses negatively charged surfaces, which promote the adsorption of Cu in the soil and form strong bonds with it. According to (Hosseinpur & Dandanmozd, 2010) ^[12], the Langmuir parameters, specifically the maximum adsorption (b) and the bonding energy constant (KL), are influenced by the chemical and physical qualities of the soil.

3.6 Maximum adsorption (X_m)

X_m represented saturation adsorption amount on the soil samples were ranged (106-20000) mg Cu.Kg⁻¹ while the X_m value for CaCO₃ (1427). This found refers clearly to the role of calcium carbonate in copper relation, due to the efficiency of copper concentration from solution to replace Ca-in CaCO₃ crystal by isomorphs substitution on owns. This foundation agree with ^[30], who found the main content of copper was in soil carbonate fraction. The adsorption constant (k) was related to adsorption energy and reflected the energy of Cu⁺² adsorbed by solid phase to a certain degree, and also this parameter reflects the affinity of (ionic species) bonding with solid matrix.

3.7 The Maximum Buffering Capacity (MBC)

The MBC value, which was equal to product of X_m and KL was conserved as the maximum buffer capacity or sorption characteristics value of Cu⁺² absorbed by soil and reflected the strength and capacity factor of Cu⁺² adsorbed by soil totally. As shown in a great number of researches that MBC values can be used to characterized, the characteristics of heavy metal adsorbed by soil. As we can see from the Table (5) MBC values of soil samples were ranged (0.02-117.5) mg Cu.Kg⁻¹ while the MBC value for CaCO₃ WAS (0.125). Large MBC value demonstrated that the adsorbed Cu⁺² was in low energy status (Which could migrated easily) and the self-purification and buffering capacity of such soil were strong. This foundation agree with 17 29) in Iraqi soils. Soils with greater MBC values have a lower requirement for Cu⁺² saturation than soils with lower MBC values. The maximum adsorption capacity provides valuable information about the interaction between the added ion and the adsorption surface, which aligns with the findings (Hooda, 2010) ^[11]. The study indicates that soil conservation measures, substitution of manure for a solution with Cu⁺² concentration, and the strength and capacity factor of Cu⁺² absorbed by the soil all impact the Maximum Binding Capacity (MBC) of ions. Evidence indicates that in clay minerals, an ion with a lower valence displaces another ion with a higher valence, resulting in a deficit of positive charge. Certain adsorption isotherms exhibit an amalgamation of chemical and physical adsorption profiles.

This phenomenon can be explained by the presence of numerous adsorption sites on the soil surface when the concentration of the solution is low. Due to the high adsorption rate and the absence of saturation, a significant quantity of adsorption occurs. The primary processes at this stage were non-specific adsorption and physical adsorption. Subsequently, the copper gradually filled the adsorption sites, causing a decrease in the adsorption rate. As a result, the adsorption-isotherm curve exhibited a more gradual slope until it eventually achieved a state of adsorption equilibrium. This process may be attributed to both selective adsorption and chemical adsorption. The rise in ion quantity and the decline in ion bonding energy in these soils result in enhanced rates of ion propagation and greater availability for plant absorption due to the adsorption surfaces in the soil solution. The elevated ion adsorption capacity and the ion's low binding energy in these soils facilitate its release from the adsorption surfaces into the soil solution. Consequently, this leads to higher rates of ion propagation and increased adsorption (Allison & Allison, 2005; Karim, 2020) ^[4, 13].

3.8 Langmuir separation factor (R_L).

Thermodynamic parameters of adsorption in Table 2 show the values of the Diffusion coefficient R_L is a dimensionless constant, with values 0.010 and 3.922 which means that copper can be readily released from the surfaces where it is adsorbed and enters the soil solution. As a result, the rates at which copper ions spread and their concentration in the liquid phase increase. This indicates that the response of the adsorbed copper is spontaneous. The R_L values observed in the examined soils ranged from 0 to 1, indicating that the exchange of Cu⁺² with the soil was advantageous for the solid phase from the liquid phase. However, soils 3 and 7 exhibited unfavorable adsorption. The R_L value might result in four different outcomes:

1. Favorable adsorption when $0 < R_L < 1$.
2. Unfavorable adsorption when $R_L > 1$.
3. Linear adsorption when $R_L = 1$.
4. Irreversible adsorption when $R_L = 0$.

The separation factor (R_L), a dimensionless constant, represents the fundamental characteristics of the Langmuir isotherm equation. This equation assumes an infinite number of sorption sites. It is more accurate in describing the behavior of a heterogeneous soil media with varying chemical and physical properties. The observed results closely aligned with the findings previously reported by (Hosseinpur & Dandanmozd, 2010; Karim, 2018; Li *et al.*, 2017; Sweed, 2019) ^[12, 4, 18, 26].

4. Discussion

The results obtained in this study found, the adsorption of Cu⁺² exhibited a positive correlation with increasing Cu⁺² concentrations in the contact solution across all soil samples. Previous studies also reported consistent findings (Allison & Allison, 2005; Hosseinpur & Dandanmozd, 2010; Karim, 2020; Kim *et al.*, 2012) ^[4, 12, 13, 15], which revealed that the soil (2) exhibited the highest adsorption of Cu⁺². In contrast, the soil (Alloway) showed the lowest adsorption, particularly when the highest level of Cu⁺² was supplied. The tested soils were arranged in the following order: soil 2, 4, 8, 5, 6, 3, 1, 7, and 9. The comparison was made concerning the presence of Calcium carbonate mineral. The largest adsorption capacity of Cu⁺² in soil may

be attributed to the elevated levels of total CaCO_3 , the maximum clay content, and a relatively high pH. Soil carbonates have a crucial role in adsorbing additional Cu (Lammers *et al.*, 2017; Lee *et al.*, 2007)^[16, 17]. The elevated pH levels led to enhanced adsorption of Cu due to the formation of Cu complexes with OH ions and an increased overall negative charge (Al-Tamimi, 2004; Mehmedany *et al.*, 2016)^[3, 20]. Additionally, the clays possess abundant sorption sites that facilitate Cu's non-exchangeable (specific) sorption. Most of the soil samples exhibited elevated pH levels (Table 1). Fig. (1) clearly illustrates the significant impact of calcium carbonate on Cu's adsorption, acting as an effective catalyst in the adsorption process. Furthermore, active CaCO_3 demonstrated greater efficacy in Cu adsorption than total CaCO_3 , which is likely attributed to the larger surface area of active CaCO_3 compared to total CaCO_3 . It has been shown that in clay minerals, an atom with a lower valence position replaces one with a higher valence, leading to a deficiency in positive charge or the formation of Cu-isotherm curves.

5. Conclusion

We concluded calcareous soils with clays regarded an excellent adsorbent material to remove copper from aqueous solutions and wastewater.

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References

1. Akrawi H, Al-Obaidi M, Abdulrahman CH. Evaluation of Langmuir and Freundlich isotherm equation for Zinc Adsorption in some calcareous soil of Erbil province north of Iraq. IOP Conference Series: Earth and Environmental Science; c2021.
2. Al-Hassoon S, Al-Hayani A, Al-Obaidi M. Copper adsorption in two different soil texture. Iraqi Journal of Agricultural Sciences. 2019;50(2):203-210.
3. Al-Tamimi H. A kinetic model for copper sorption processes of the calcite surface. II. Distribution coefficient for solid solution. Basrah Journal of Sciences. 2004;22(1):23.
4. Allison JD, Allison TL. Partition coefficients for metals in surface water, soil, and waste. Rep. EPA/600/R-05; c2005, p. 74.
5. Alloway BJ. Bioavailability of Elements in Soil 15. Essentials of Medical Geology; c2002, p. 351.
6. Alloway BJ. Sources of heavy metals and metalloids in soils. Heavy metals in soils: trace metals and metalloids in soils and their bioavailability; c2013, p. 11-50.
7. Babel S, Kurniawan TA. Low-cost adsorbents for heavy metals uptake from contaminated water: A review. Journal of hazardous materials. 2003;97(1-3):219-243.
8. Bashir MA, Rehim A, Liu J, Imran M, Liu H, Suleman M, *et al.* Soil survey techniques determine nutrient status in soil profile and metal retention by calcium carbonate. Catena. 2019;173:141-149.
9. Das B, Mondal N, Bhaumik R, Roy P, Pal K, Das C *et al.* Removal of copper from aqueous solution using alluvial soil of Indian origin: equilibrium, kinetic and thermodynamic study. J. Mater. Environ. Sci. 2013;4(4):392-409.
10. Hong K-S, Lee HM, Bae JS, Ha MG, Jin JS, Hong TE, *et al.* Removal of heavy metal ions by using calcium carbonate extracted from starfish treated by protease and amylase. J. Anal. Sci. Technol. 2011;2(2):75-82.
11. Hooda PS. Assessing bioavailability of soil trace elements. Trace elements in soils; c2010, p. 227-265.
12. Hosseinpour A, Dandanmooz F. Sorption characteristics of copper in some calcareous soils of western Iran. American Journal of Science. 2010;6(11):103-108.
13. Karim KH. Copper adsorption behaviour in some calcareous soils using Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models. Journal of Soil Sciences and Agricultural Engineering. 2020;11(1):27-34.
14. Karim M. Optimization of Fly-Ash to Soil Mix Ratio and Curing Period for Subgrade Use. Insight-Civil Engineering; c2018.
15. Kim JG, Jung MY, Park SJ, Rijpstra WIC, Sinninghe Damsté JS, Madsen EL, *et al.* Cultivation of a highly enriched ammonia-oxidizing archaeon of thaumarchaeotal group I. 1b from an agricultural soil. Environmental Microbiology. 2012;14(6):1528-1543.
16. Lammers LN, Bourg IC, Okumura M, Kolluri K, Sposito G, Machida M. Molecular dynamics simulations of caesium adsorption on illite nanoparticles. Journal of Colloid and Interface Science. 2017;490:608-620.
17. Lee M, Paik IS, Kim I, Kang H, Lee S. Remediation of heavy metal contaminated groundwater originated from the abandoned mine using lime and calcium carbonate. Journal of hazardous materials. 2007;144(1-2):208-214.
18. Li F, Zhang J, Jiang W, Liu C, Zhang Z, Zhang C, *et al.* Spatial health risk assessment and hierarchical risk management for mercury in soils from a typical contaminated site, China. Environmental Geochemistry and Health. 2017;39:923-934.
19. Lü C, Yan D, He J, Zhou B, Li L, Zheng Q. Environmental geochemistry significance of organic phosphorus: An insight from its adsorption on iron oxides. Applied Geochemistry. 2017;84:52-60.
20. Mehmedany LA, Hashim FA, Barwari VI. Adsorption behavior of copper in some calcareous soils from Duhok Governorate. Science Journal of University of Zakho. 2016;4(2):200-207.
21. Rashad M, Eldin MM, Abd El Latif M. Thermodynamic approach for copper and cadmium specific and non-specific adsorption on calcareous soil-biopolymer composite. Alexandria Engineering Journal. 2005;44(3):469-476.
22. Shaheen SM, Tsadilas CD, Rinklebe J. A review of the distribution coefficients of trace elements in soils: Influence of sorption system, element characteristics, and soil colloidal properties. Advances in colloid and interface science. 2013;201:43-56.
23. Soares MR, Alleoni L. Distribution coefficient (KD) of heavy metals in Brazilian soils. 18th World Congress of Soil Sciences; c2006.
24. Song N, Lee Y, Lee M. Remediation process by using lime and calcium carbonate for heavy metal contaminated groundwater originated from landfills; c2005.

25. Sparks D. Methods of soil analysis. Soil Science Society of America. 5585 Guilfords Rd. Madison, WI; c2017, p. 537.
26. Sweed AAA. Impact of certain organic wastes on some isotherm models of copper and nickel adsorption on a loamy sand soil. Egyptian Journal of Soil Science. 2019;59(4):353-362.