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The Kinetic Study of Adsorption of Copper Metal Ion in Selected Contaminated Red Soil Samples in Palestine

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Abstract: Heavy metals are persistent pollutants in the environment. Problems associated with the cleanup of sites contaminated by metals have demonstrated the need to develop remediation technologies that are feasible, quick, and effective in a wide range of physical settings. In this study we have investigated the adsorption of Cu(II), onto red soil in single and multi-element systems as a function of soil and heavy metal concentrations. Before contamination, soils were characterized to determine particle size, pH, organic matter content and heavy metal contents. The results of experimental sorption data fitted very well the Freundlich isotherm model with $n = 1.4$ and $k = 1.25$ and first order kinetics model. The best pH for adsorption of Cu^{2+} on red soil was found to be 4.0. Adsorption of metals on soil increased in the order $\text{Cu} > \text{Pb} > \text{Zn} \approx \text{Cd}$. This trend might be related to the increase in the electronegativity of the metal ion.

Key words: Adsorption, contaminants, kinetics, isotherm, pollutants, remediation.

1. Introduction

Heavy metals are one of the most important and frequent soil and sediment contaminants [1]. Jaffe et al. [2] found significant amounts of various trace metals, including zinc (Zn), lead (Pb), cadmium (Cd), chromium (Cr) and cobalt (Co), along with petroleum hydrocarbons, PAHs, and chlorinated hydrocarbons in marine sediment. They noted that important sources of contamination include industrial and agricultural activities. According to Ho and Hui [3], high levels of Polychlorinated biphenyls (PCBs), Poly aromatic hydrocarbons (PAHs), as well as copper (Cu) and Zn were found in river sediments in an industrial area surrounded by a densely populated area, suggesting that the sources of contamination are related to human activities, such as domestic and industrial discharges, agricultural chemical applications and soil erosion.

Heavy metals are presently washed from contaminated soils with organic/inorganic acids,

chelating agents and surfactants [4-6]. Acids can extract metals from soils since metals become mobile when the soil pH drops under 6.0.

In soils, heavy metal ions can be present as soluble compounds like ions and metal complexes or as exchangeable forms. However, heavy metals are generally rendered immobile by associating with different soil fractions and compartments such as carbonate, oxide, hydroxide, organic matter and residual materials [7, 8]. The mobility of heavy metals is often affected by various factors including pH, redox potential, nature of soil components and cation exchange capacity (CEC). In the case of hydrophobic contaminants, soil organic matter (SOM) is mainly responsible for the sorption of contaminants, particularly those which are nonionic in nature. Since they have relatively little impact on the soil environment compared to strong acid and chelating agent, surfactants are promising agents for the remediation of soils contaminated by either heavy metals or organics. However, one type of surfactant alone can only effectively desorb a single type of

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contaminant, either hydrophilic heavy metals or hydrophobic organics.

The more specific research objectives pertain to the remediation of soils contaminated with heavy metal like copper, is to study the effect of soil concentration on the adsorption of heavy metals on soil and to establish which kinetic model best reproduces the complexation of heavy metals from a red contaminated soil, as well as the effect of pH on adsorption of metal ion on red soil.

2. Experiment and Materials

2.1 Soil Sampling and Characterization

Soil samples of most common soils of Palestine were selected for the study. The soils were identified and classified based on sieve analysis and hydrometer test (ASTM H-152). The organic matter of the soil was determined by chromic acid method [9], the electrical conductivity was measured using conductivity meter (IS 2720-part 21, 1977). Total soluble solids were estimated from electrical conductivity, the soil pH was measured using a direct reading type pH meter (JENWAY 3540 PH & Conductivity Meter) with glass electrode and calomel reference electrode. The specific gravity was determined by pycnometer method (IS 2720-part 3/sec 1, 1987). The moisture percentage of each soil was determined, and taken into account when an exact weight is required for analysis. The properties of the collected soils are given in Table 1. Soils were sieved through IS (International Standard) sieve No. 40 (0.42 mm aperture as per IS 2720-part 4, 1987). The fraction passing through the sieve was collected and preserved in air tight plastic containers for further studies.

2.2 Cleaning Soil

A special column was prepared for this purpose (50 cm long with a radius of 2.5 cm with a stopcock to control the rate flow of washing solution). In each column 200 g of soil was washed by 500 mL of distilled water followed by 500 mL of 0.1 M perchloric (which

Table 1 Properties of different soils used for the present study.

Soil properties	Red Soil	Calk Soil	Sandy Soil
specific gravity (g/cm ³)	2.5	2.2	2.7
pH value *	8.5	7.1	8.5
Electrical conductivity (Ec), (μs)	230.0	184.1	84.5
Clay (%)	39.0	46.0	2.0
Silt (%)	61.0	54.0	3.0
Organic matter (%)	9.6	8.4	0.3
Moister content (%)	8.0	2.0	0.2

*The soil pH was determined by shaking 5 g of air-dry soil with 10 mL of deionized water for 60 min, letting the solution rest overnight, and then measuring the solution with a pH meter.

is suitable for Beckman flame Atomic Absorption [10]) acid then 500 mL of distilled water. The soil was dried at 95 °C for 24 hours using universal ovens (memmert UNB 100-500, U B 400-500).

A 1.0 g of soil was digested with concentrated nitric acid (Method 3050A, Acid Digestion of Sediment, Sledges', and Soil by Neil Wilson 9/5/95) and tested for elemental analysis. No metals (Cu²⁺, Cd²⁺, Zn²⁺ and Pb²⁺) were present in the cleaned soil.

2.3 The Effect of pH on the Adsorption of Copper Ions on Red Soil at Room Temperature (25 °C)

In this experiment the adsorptive behavior of Cu²⁺ on red soil at different pH values, as shown in Fig. 1, was studied. For this study 10.0 g of red soil were replaced in 330-mL glass stoppard bottles. After that, 100 mL of copper solution with a concentration of 125 ppm was added to the bottles at different pH values. The initial pH of the sorbate (metal solution) was adjusted for each set of the experiment by adding 0.1 M HCl or 0.1 M NaOH.

The soil sample has been shaken in a shaker for 24 hours at constant temperature and then left for additional 24 hours. A 10 mL of supernatant solution was centrifuged at 2500 rpm for 15 minutes.

The amount of metal sorbed by the soil was calculated from the initial metal concentration of the solution and metal content of the supernatant after the specified period 24 hours of shaking (This procedure was repeated twice for each experiment).

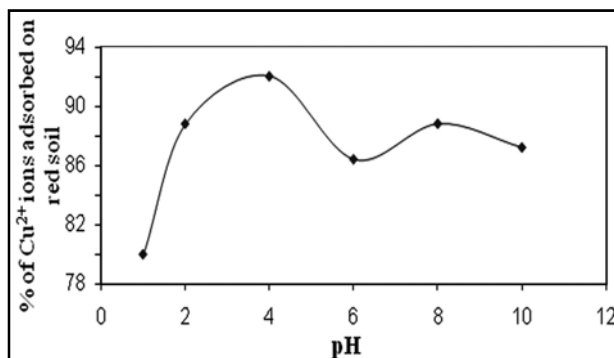


Fig. 1 Adsorption of copper on red soil at different pH values.

3. Results and Discussion

3.1 The Effect of Soil Concentration on the Adsorption of Copper Ions on Red Soil

To study the effect of soil concentration on the adsorption of heavy metals on red soil, various concentrations of red soil ranging between 0.0 to 10 g/100 mL were allowed to adsorb Cu²⁺ ions from 50 ppm copper nitrate solution for 72 hours. These results are summarized in Fig. 2. These results indicate that increasing soil concentration will increase the uptake of copper from the solution. This agrees with previous results on the adsorption of lead on river mud by Salim and Cooksey [11].

3.2 The Effect of Copper Concentration on the Adsorption of Copper Ions on Red Soil

To study the kinetic sorption of copper on red soil a set of experiments were done to measure the adsorption of three concentrations of copper (50 ppm, 40 ppm and 30 ppm) with time in order to calculate the rate of adsorption in each concentration of copper in solution and hence to find the reaction order of the adsorption process and finally to apply the Freundlich and Langmuir adsorption isotherms on the results [11, 12]. The results of these experiments are shown in Table 2.

Order of reaction:

For each initial concentration of copper shown on the Table 2, graph was plotted between the concentrations of copper adsorbed on red soil C_s (mg/g) against $t^{1/2}$ (hour). The graphs were straight lines and

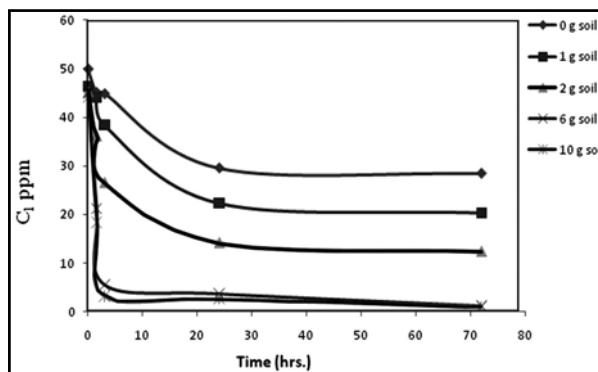


Fig. 2 The effect of soil concentration on the adsorption of copper ions on red soil from 50 ppm copper solution.

from the slopes of these lines (i.e. $dC_s/d\sqrt{t}$), the rate of adsorption (dC_s/dt) was calculated from the formula:

$$(dC_s/dt)_t = \frac{1}{2\sqrt{t}}(dC_s/d\sqrt{t}).$$

$$\text{Rate} = (dC_s/dt)_t = (1/(2\sqrt{t})) \times (dC_s/d\sqrt{t})_t = 0.0633 \text{ ppm/g/hour}$$

$$\text{Slope} = 0.633 = dC_s/d\sqrt{t} \text{ at } 40 \text{ ppm}$$

$$\text{Rate} = (dC_s/dt)_t = (1/(2\sqrt{t})) \times (dC_s/d\sqrt{t})_t = 0.183 \text{ ppm/g/hour}$$

$$\text{Slope} = 0.041 = dC_s/d\sqrt{t} \text{ at } 30 \text{ ppm}$$

$$\text{Rate} = (dC_s/dt)_t = (1/(2\sqrt{t})) \times (dC_s/d\sqrt{t})_t = 0.0118 \text{ ppm/g/hour}$$

Plotting the rate of adsorption of copper (dC_s/dt) against concentration of copper in solution (C_i) gives a straight line, Fig. 3.

From Fig. 3, it was shown that the rate of adsorption of copper is proportional to the concentration of copper remaining unadsorbed at a certain time, irrespective of the initial concentration of copper in solution. Therefore, it can be concluded that the adsorption process of copper on red soil is a first order reaction with respect to copper. A similar conclusion was reported by Augustine et al. [12].

4. Application of the Adsorption Isotherms

The Freundlich and Langmuir adsorption isotherms are the most widely applied isotherms for the adsorption of metal ions on a wide variety of adsorbents.

To apply the Freundlich Equation on our work various concentrations of copper ranging between 10-300 ppm were adsorbed at constant weights of red

Table 2 Adsorption of copper ions on red soil.

t, h	$t^{1/2}$, h	Cu^{2+} (50 ppm)		Cu^{2+} (40 ppm)		Cu^{2+} (30 ppm)	
		C_s (mg/g)	C_i (ppm)	C_s (mg/g)	C_i (ppm)	C_s (mg/g)	C_i (ppm)
1.0	1.0	46.7	3.3	34.0	6.0	28.5	1.5
3.0	1.7	46.9	3.1	34.5	5.5	28.6	1.4
12.0	3.5	47.2	2.8	35.5	4.5	28.7	1.3
24.0	4.9	47.5	2.5	36.3	3.7	28.8	1.2
72.0	8.5	48.4	1.6	38.8	1.2	28.9	1.1

C_s : Concentration of copper adsorbed on soil.

C_i : Concentration of copper remaining unabsorbed in solution.

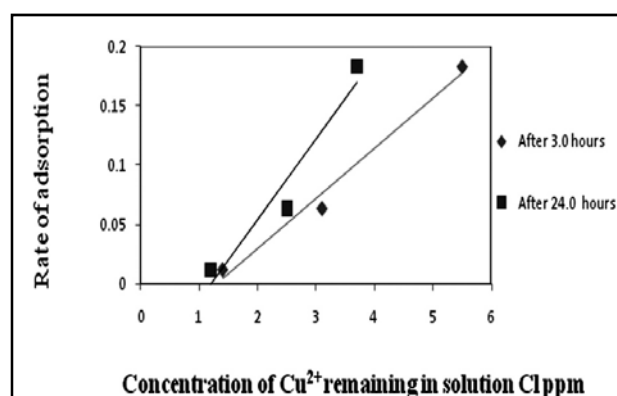


Fig. 3 The dependence of the rate of copper adsorption on red soil on the concentration of copper remaining in solution after 3 and 24 hours.

soil for 24 hours. The results are shown in Fig. 4. A straight line obtained in Fig. 4 shows that the results agree with the Freundlich Equation.

$$\log C_s = \log K + \frac{1}{n} \log C_i$$

Where C_s is the concentration of Cu^{+2} adsorbed on red soil and C_i is the concentration of Cu^{2+} remained in solution. K and n are constants. From Fig. 5 the values of n and K are 1.4 and 1.25 respectively.

The Langmuir adsorption isotherm is commonly applied to monolayer chemisorption of gases. However, several authors have applied this isotherm for the adsorption of metal ions on sorbents. This isotherm is mainly applied when no strong adsorption is expected and when the adsorption surface is uniform.

A commonly used formula of the Langmuir adsorption isotherm is:

$$1/C_s = 1/b + 1/ab (1/C_i)$$

Where C_s , C_i are defined in the Freundlich Isotherm and a is the constant indicative of the bonding energy

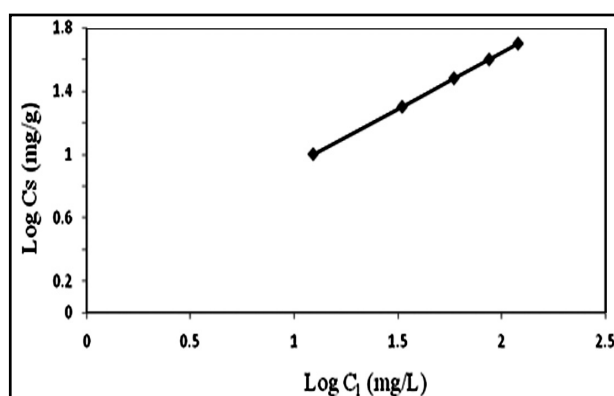


Fig. 4 The application of the Freundlich equation for the adsorption of copper on red Soil after 24 hours.

between the adsorbent and the adsorbed species and b the constant indicative of the mass of the adsorbed species required for a monolayer converge of a unit mass of adsorbent.

Both the Freundlich and Langmuir adsorption isotherms showed linear relationship on the present results shown in Figs. 4 and 5, for the Freundlich and Langmuir adsorption isotherms, respectively. The parameters of the Freundlich adsorption isotherm were calculated from the results of Fig. 4. The value of parameter n is equal to 1.4 ($n \sim 1$), indicating a low coverage of copper on red soil. The value of this parameter shows also the decrease of the intensity of adsorption of copper with decreasing efficiency of removal of copper by washing solutions.

The value of the parameter K also indicates decreasing efficiency of removal of copper by normal washing solutions.

The parameters of the Langmuir adsorption isotherm, a and b , were found to be erroneous and with negative

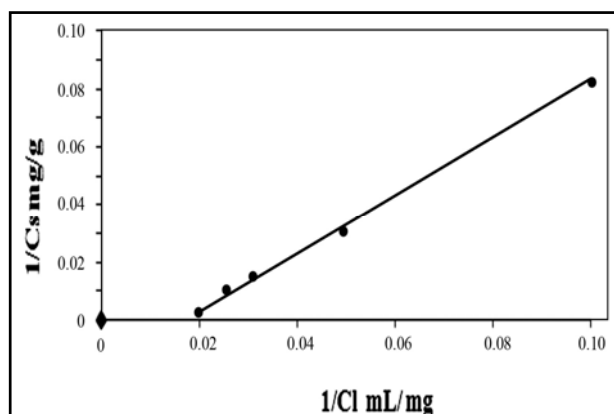


Fig. 5 The application of Langmuir isotherm for the adsorption of copper on red soil after 24 hours.

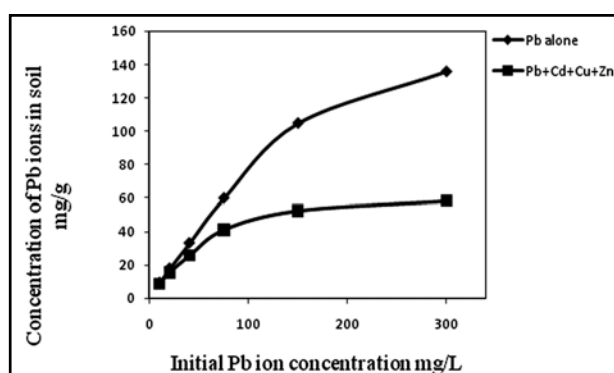


Fig. 6 Adsorption of lead ions (50 ppm) on red soil with single (Pb^{2+}) and multi metal ions (Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+}) at soil concentration equal 1.0 g/100 mL.

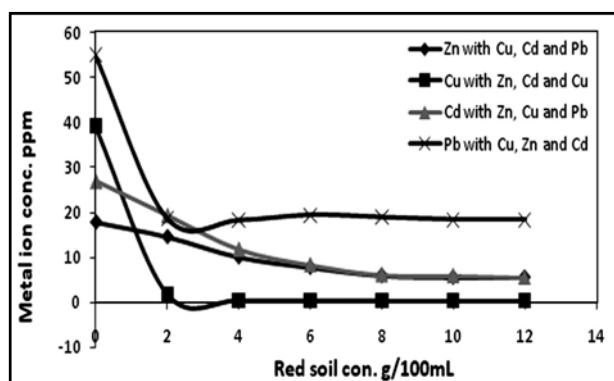


Fig. 7 Adsorption of metal ions on red soil from 100 mL of 50 ppm of four metal ions (Pb^{2+} + Cu^{2+} + Zn^{2+} + Cd^{2+}) in solution.

values (where a is equal to -73.45 and b is equal to 1.08). This suggests the unsuitability of this isotherm for application on the present results. The negative values of the Langmuir parameters can be attributed to the non-uniformity of soil particles surfaces and to the high strength of adsorption of copper on red soil. These

results agree with the conclusions of Salim and Cooksey [11]; Augustine et al. [12], Barrow [13] and Jiang et al. [14].

4.1 Rate-Limiting Step

Adsorption of metal ions on soil particles follows a three-step process [15]:

(1) Film diffusion: in which metal ion reach by diffusion, driven by concentration gradient, the surface of soil particles.

(2) Intra-pore diffusion: in which most of the adsorbed metal ions have to enter the pores of the soil particles in order to reach the internal adsorption sites.

(3) Adsorption: in which the metal ions become adsorbed on the adsorption sites.

The straight line relations found between C_s and \sqrt{t} suggest that the diffusion is the rate limiting step. The same conclusion was also suggested for the uptake of cadmium on beach leaves [15].

4.2 The Effect of Competitive Ions on the Adsorption of Heavy Metals on Red Soil

The effect of presence of competing ions on the adsorption of metal ions on red soil was studied using the ions Pb, Cu, Zn and Cd.

The adsorption of each metal ion on red soil was examined alone and in presence of the other ions. Two types of study were done, first study was done at constant metal ion concentration (50 ppm) and variable red soil concentration (0-12g/100 mL), and the second study was done at constant red soil concentration and variable copper ion concentration (10-300 ppm). The results of these two types of experiments are shown in Fig. 6.

When increasing the initial metal ion concentration from 10 to 300 ppm and from 2.0 to 12 g/100 mL of soil resulted in, an increase in the metal ion adsorbed for both single metal and multi-metal ions competitive adsorption was shown.

When the initial concentration of Pb was 10.0, and 20.0 ppm like in Fig. 6 more than 90% of lead ions was adsorbed. At higher concentrations (150 ppm) 70% of Pb were adsorbed onto the red soil in single metal

compared with 35% of Pb ion adsorbed from multi-metal competitive adsorption. This may be attributed to the presence of a large number of adsorption sites which were available to the metal ions at low concentrations and the competition on these sites is obvious at high concentrations, the same results was reported by Bhattacharyya and Gupta [16].

Finally, Fig. 7 shows the summing of four metals Copper, Zinc, Cadmium and Lead. Concerning the main question of the competitive adsorption mechanism, the batch experiment results have clearly shown a different behavior of heavy metals in the four studied metals. In fact, for red soil Cu has clearly shown the highest adsorption rate as compared to Cd, Pb and Zn, as shown in Fig. 7. A similar conclusion was reported by McBride [17] and Alcacio et al. [18]. For adsorption isotherms, the selectivity sequence was $\text{Cu} > \text{Pb} > \text{Zn} = \text{Cd}$ in single-element systems and $\text{Pb} > \text{Zn} = \text{Cd} > \text{Cu}$ in multi-element systems, Fig. 7.

The extended constant-capacitance surface complexation model by Srivastava et al. [19] proposed three kinds of possible reaction mechanism to explain the adsorption behavior.

At low pH, all these metals adsorb onto permanent charge sites by ion exchange reactions. Adsorption onto variable charge sites takes place at higher pH by forming inner-sphere complexes at the crystal edges and octahedral alumina faces. The hydroxyl species of Cu and Pb adsorb by forming monodentate inner-sphere complexes, were adsorption of Cd and Zn on variable charges occurs by forming bidentate complexes.

Permanent-charge minerals such as montmorillonite carry a negative charge as a result of ion substitution during the formation of the minerals variable-charge minerals such as Fe, Mn, and Al oxides carry charges varying from negative to positive, depending on pH.

Adsorption and desorption of Cu^{2+} on soil are affected by the proportion of these two types of minerals. Moreover, the Fe, Al, and Mn oxides have a relatively strong affinity (pH dependent) for Cu^{2+} and other heavy

metal cations and the adsorption of Cu^{2+} on these oxides is considered to be inner-sphere complex through a chemisorption process [20]. On the other hand, soil organic matter has a strong affinity for Cu^{2+} at low levels of Cu^{2+} [21].

Recently, Alcacio et al. [18] provided spectroscopic evidence for the hypothesis proposed by McBride [22], for the possible binding configurations of Cu^{2+} on complexes of oxide minerals and organic matter: (i) Cu^{2+} is bonded to the mineral surfaces only (inner-sphere complex); (ii) Cu^{2+} is bonded to the organic matter that is adsorbed by the oxides at high levels; and (iii) Cu^{2+} acts as a bridge cation between the oxides and the organic matter that is adsorbed at low levels. Therefore, Fe, Al, and Mn oxides and organic matter are considered to play a very important role in the adsorption-desorption of Cu^{2+} in the variable-charge soil.

5. Conclusions

Adsorption of Cu^{2+} on red soil of Palestinian soil was studied and the results were obtained:

The uptake of copper from red soil was increased by increasing soil concentration.

The order of adsorption of heavy metals on soil was first order reaction with respect to copper ions.

Our results agree with Freundlich and Langmuir Isotherms indicating a low coverage of copper on red soil.

The competition of the studied heavy metals on adsorption on red soil is not present at low concentrations of target metals, but at higher concentrations the main factor control the competition of heavy metals is electronegativity.

The best pH for adsorption study of heavy metals is 4.0.

Recommendations for Further Work:

- (1) The soil can be replaced by olive jeft after chemical treatments.
- (2) This technique can be used for other different heavy metals and toxic anions like nitrates.

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