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Behavior and mechanism of various components of soil in Cu (II) adsorption from aqueous solution

Haniyeh Jalayeri[a,*], Mohammad Mehdi Salarirad[b], Mansour Ziaii[a]

[a]*Department of Mining, Petroleum and Geophysics Engineering, Shahrood University of Technology, Shahrood, Iran, Tel. +98 2332392204; emails: haniyeh.jalayeri@gmail.com (H. Jalayeri), mziaii@shahroodut.ac.ir (M. Ziaii)*
[b]*Department of Mining and Metallurgy Engineering, Amirkabir University of Technology, Tehran, Iran, Tel. +98 2164542974; Fax: +98 2166405846; email: salari@aut.ac.ir*

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ABSTRACT

Soil plays a significant role in control of heavy metals in the environment. Therefore, understanding of the adsorption properties of soil is essential in solving pollution problems. The aim of this paper is to study Cu (II) adsorption onto two soil samples taken from around Sarcheshmeh copper mine (i.e. SA and SE). Also, the adsorption isotherms of Cu (II) onto soil samples were studied. The Langmuir isotherm indicated the best fit for the experimental data in comparison with other isotherms such as Freundlich and Temkin. The capacity of Cu (II) adsorption was assessed by distribution coefficient (K_d) for soil samples that SA sample showed high K_d values. Sequential extraction was conducted for the evaluation of main sorbents of Cu (II) in soils. The results of sequential extraction were indicated and demonstrated that carbonate phase in SA and SE samples play a significant role in the adsorption of Cu (II) metal. In this study, scanning electron microscopy was used to evaluate the relationship between clay content of soil and adsorption process.

Keywords: Soil; Adsorption isotherms; Distribution coefficient; Sequential extraction; X-ray energy dispersive spectroscopy

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1. Introduction

Mining activities led to production of large volume of acid mine drainage (AMD), especially in sulfide ores. AMD generally contains highly toxic heavy metals which may have harmful effects on the environment [1]. At Sarcheshme copper mine (SCM), Iran, the AMD formed contains high copper concentrations [2]. Although copper is essential to human life and health, but similar to all heavy metals it is potentially toxic as well [3]. Drinking water containing more than 1.0 mg/L of Cu (II) may cause hemochromatosis and gastrointestinal catarrh diseases due to their accumulation in liver and kidney [4].

The interaction of soil and wastewater is a key element in nature due to its important role in adsorption and immobilization of heavy metals. The capacity of soils to adsorb heavy metals from aqueous solution is considerable and it significantly mitigates environmental issues. Adsorption is a main process in natural attenuation of potentially toxic metals from wastewaters and it is also studied for understanding of how metals are transferred from a liquid phase to the surface of a solid phase [5,6]. The adsorption ability of

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*Corresponding author.

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soils depends on a set of properties such as pH and the presence of adsorption sites in various soil components as carbonates, organic matter, clay minerals, and Fe and Al (hydr) oxides [7–9].

Distribution of metals between soil and solution at equilibrium can be assessed by distribution coefficient (K_d). Mobility and retention of heavy metals in soil can be related to their distribution coefficients. K_d is the valuable parameter for investigating the adsorption capability of different soils [10–15].

Adsorption isotherms describe the adsorption data in batch experiments. The capability of soil adsorption can be obtained by analysis of isotherms. However, the information achieved from adsorption isotherms is not sufficient because the interactions of heavy metals with soil are not clear and the actual portioning of metals in various fractions of soil cannot be defined [7]. Thus, procedures such as sequential extraction can be combined with research on adsorption isotherm. Sequential extraction procedures are widely used to study heavy metals portioning in various soil components [16,17]. This method obtains metals sorbed in various soil phases during adsorption process.

Sarcheshmeh copper deposit is one of the largest copper mine in the world. In fact, this area involves an important mining site with industrial activities which lead to environmental contamination by heavy metals. The towns surrounding mining district were affected by contamination. Recently, some researches have been conducted on the AMD and its detrimental environmental effects and also about environmental geochemistry of heavy metals in soils around Sarcheshmeh porphyry copper mine and AMD treatment [2,18,19]. No studies have been conducted on heavy metals adsorption by soil at SCM and the adsorption capability of *in situ* soil was not evaluated previously. Soils involve various fractions which are strongly capable to adsorb heavy metals and can be used as low-cost adsorbent. This study is very essential in this mining site in order to estimate efficiency of soil for heavy metals attenuation. The remarkable point in this study is the profiting from scanning electron microscopy (SEM)–energy dispersive spectroscopy (EDS) to find a relationship between adsorption process and Cu (II) distribution in soil.

This report studies adsorption of Cu (II) onto soil surrounding SCM. The main objectives of this work are as follows: (a) to evaluate Cu (II) adsorption capability of soil in this site; (b) to investigate Cu (II) adsorption isotherms; (c) to identify distribution coefficients; (d) to determine adsorbed Cu (II) portioning in various soil components by sequential extraction; and (e) to assess adsorption process by SEM.

2. Material and methods

2.1. Soil samples and analysis

The soil samples were collected from SCM surrounding area, 160 km SW of Kerman. Previous researches in this area showed that there is a level of heavy metal pollution in the soil. Two sample sites were selected and five samples, approximately 6 kg in each site, were collected from the surface layer (0–20 cm). Soil samples (SA and SE) were packed and were transported to the laboratory. All samples were air dried and sieved through 2 mm mesh and were homogenized prior to soil characterization and adsorption studies. The samples were analyzed for organic carbon (OC) content [20], pH [21], cation exchange capacities (CEC) [22], oxides contents [23], $CaCo_3$ content [24], and the particle size distribution [25]. Metal concentrations in the soil were determined by ICP–OES. The soil characteristics are summarized in Table 1. The mineralogy of the clay minerals in SA and SE is illustrated by the X-ray diffraction (XRD) in Fig. 1. The most important minerals of SA soil that are identified by XRD are quartz, albite, muscovite, montmorillonite, and illite. The major peaks of SE are related to quartz, hematite, albite, illite, clinochlore, and muscovite.

2.2. Adsorption experiments

Batch adsorption experiments were carried out in fractions smaller than 2 mm. The initial Cu (II) concentrations of experimental solutions were 30, 40, 50, 70, and 100 mg/L. Five hundred milliliter of experimental solutions were placed in 2.5 L glass bottles containing initial Cu (II) concentrations 30, 40, 50, 70, and 100 mg/L and also pH 4 were adjusted. About 5 g homogenized soil was taken from the samples for the study of adsorption process. Then, it was added to 500 mL of aqueous Cu (II) solutions. The bottles were rolled at a constant rotation of 100 rpm for 24 h in order to reach the equilibrium. Sampling was performed at various determined time intervals. The Cu (II) concentration was analyzed using atomic absorption spectrophotometer (AAS). The concentration of Cu (II) retained on the soil was calculated according to Eq. (1).

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of metals in solution,

Table 1
Characteristics of soils

Soil	OC (%)	pH	CEC meq/100 g	Fe_2O_3 (%)	MnO (%)	Al_2O_3 (%)	$CaCO_3$ (%)	Clay (%)	Silt (%)	Sand (%)
SA	0.33	8.03	4.21	1.7	0.11	4.5	0.5	16	38	46
SE	0.29	7.04	6.38	2.8	0.12	4.4	0.26	18	26	56

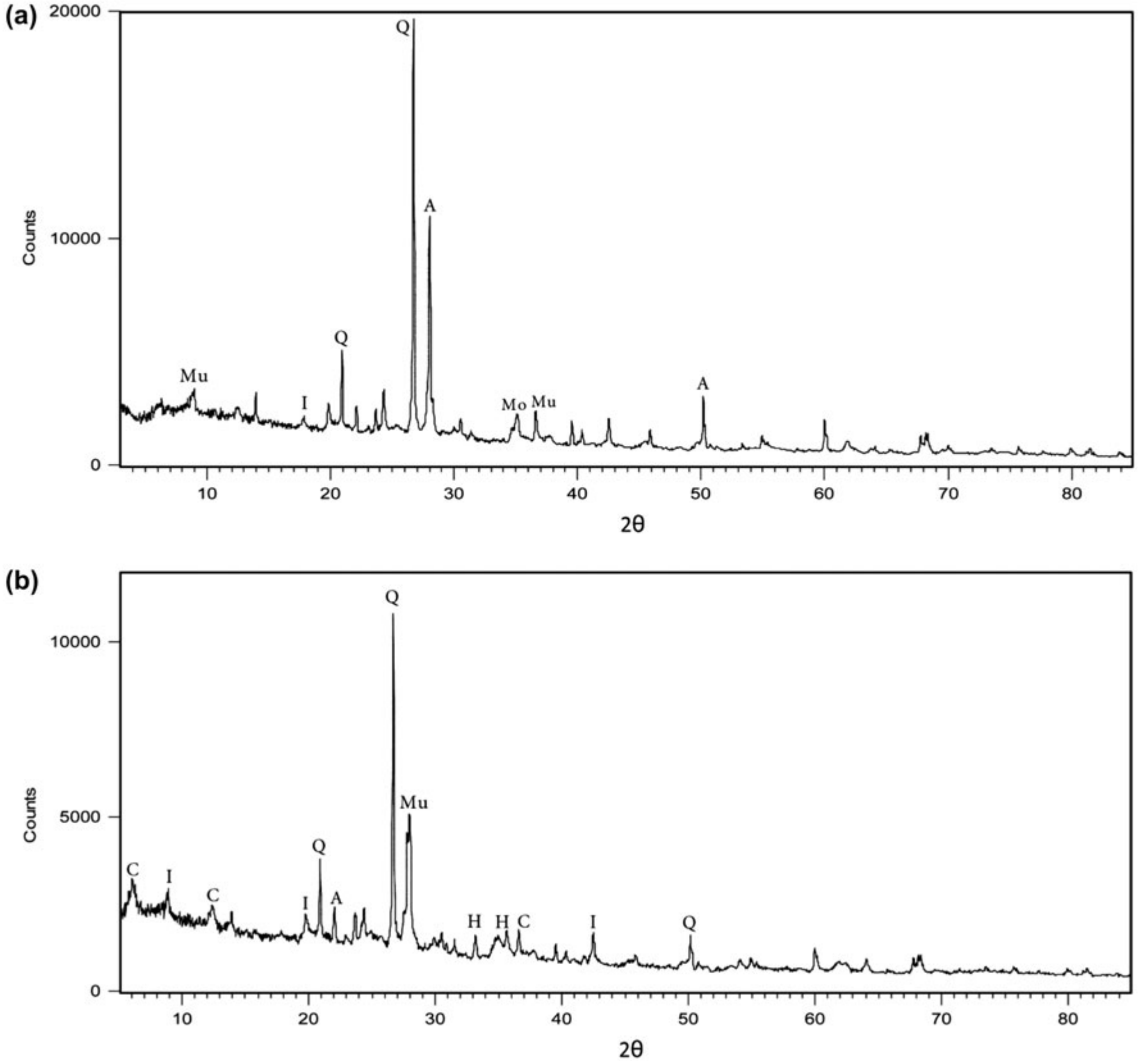

Fig. 1. XRD patterns of (a) SA sample and (b) SE sample. Q: quartz, A: albite, C: clinochlore, H: hematite, I: illite, Mo: montmorillonite, and Mu: muscovite.

respectively. V and W represent volume of the solution (L) and mass of the sorbent (g), respectively.

For each soil, adsorption capacities for Cu (II) were compared using the estimated distribution coefficients (K_d). Adsorption data were collected and then K_d for the metals in each soil at equilibrium was calculated [26] using the following expression:

$$K_d = \frac{\text{concentration of metal sorbed (mg/L)}}{\text{concentration of metal in solution (mg/L)}} \quad (2)$$

The initial Cu (II) concentration of SA and SE soil was determined by ICP-OES, as 270 and 1,325 ppm. In order to evaluate effect of Cu (II) content of soil on the solution, adsorption test was conducted using 500 mL distilled water at pH 4 and 5 g of soil samples. The obtained results from the analysis of the solution after 24 h showed that the copper ions have not entered the solution. Therefore, the Cu (II) concentration in soil has not been considered in the measured values of q_e.

2.3. Error function

Average relative error (ARE) has been calculated between experimental and calculated data [27]. ARE was calculated by:

$$\mathrm{ARE} = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{q_e^{\exp} - q_e^{\mathrm{cal}}}{q_e^{\exp}}\right| \tag{3}$$

where $q_e^{\exp}$ and q_e^{cal} are experimental and calculated adsorbate concentration at equilibrium state and N is the number of experiments. Commonly, lower ARE beside high R^2 values can be a good criterion for choosing the best-fit model.

2.4. Sequential extraction

Sequential extraction of soil samples is based on the protocol of Tessier et al. [28]. Sequential extraction was conducted to evaluate the speciation of metals. The five extraction steps were as follows:

1. Exchangeable fraction (continuous agitation with 1 M Na OAc at pH = 8.2 during 1 h).
2. Carbonate bound (continuous agitation with 1 M Na OAc adjusted to pH = 5 acetic acid during 5 h).
3. Iron and manganese oxides bound (0.04 M $NH_2OH * HCl$ in 25% (v/v) acetic acid).
4. Organic matter bound (30% H_2O_2, 0.02 M HNO_3, 3.2 M CH_3COONH_4 in 20% HNO_3).
5. Residual (HNO_3, $HNO_3 + HClO_4$, 6 M HCl).

After adsorption process, the soil samples were filtered and they were dried at the ambient temperature and homogenized afterward. A sample of 1 g each was taken using cone and quartering method and was placed in a 50 mL polypropylene centrifuge tube. After reaction with the appropriate reagent of each step, the mixture was centrifuged in order to separate the supernatant and the residue. The supernatant was analyzed by AAS, whereas the residue was washed with deionized water and dried prior to the next step.

2.5. Scanning electron microscopy

Surface morphology of these samples was studied using a Philips XL30 SEM system. A mapping of the surface was carried out by the X-ray EDS to determine the distribution of Cu (II) in soils. Information about morphology and surface topography of soil samples was observed in a scanning electron microscope. For this purpose, the samples were coated by a gold film.

3. Results and discussion

3.1. Adsorption results

An equilibrium isotherm expresses the relation between the amounts of adsorbate removed from solution at equilibrium by unit of adsorbent mass at constant temperature. The Langmuir, Freundlich, and Temkin isotherms were applied in this study. The Langmuir isotherm is described for monolayer adsorption onto a homogenous surface containing a finite number of identical sites [29–31]. The model assumes uniform energies of adsorption onto the surface [32]. The Freundlich isotherm is used to illustrate multilayer adsorption onto a heterogeneous surface with a non-uniform distribution of energies of adsorption over the surface [33]. Values K_f and $1/n$ are Freundlich constants related to capacity and intensity of adsorption, respectively. The lower fractional value of $1/n$ between 0 and 1 indicates that weak adsorptive forces are effective on the surface [34]. The Temkin model assumes that adsorption heat of all molecules in the layer would decrease linearly with coverage [35].

Langmuir isotherm model can be linearized into at least five different types as shown in Table 1. The relative parameters of five different linearized forms of Langmuir isotherm were obtained from the plots between [C_e/q_e vs. C_e], [$1/q_e$ vs. $1/C_e$], [q_e vs. $1/C_e$], [q_e/C_e vs. q_e], and [$1/C_e$ vs. $1/q_e$]. Also, the relative parameters of Freundlich and Temkin were obtained from the plots between [$\ln(q_e)$ vs. $\ln(C_e)$] and [q_e vs. $\ln(C_e)$], respectively. Linear expression of these isotherm equations and the way to obtain the isotherm parameters are given in Table 2.

Although these isotherms do not clear the adsorption mechanism, they are useful for providing information on the adsorption potential of adsorbant. The experimental data were compared to Langmuir, Freundlich, and Temkin equilibrium equations. The applicability of each isotherm to describe the adsorption process was identified by the correlation coefficients (R^2 values). The values of parameters and correlation coefficients, and ARE were listed in Table 3.

Table 2
Isotherms and their linearized expressions

Isotherms	Equations	Linear expression	Plot	Parameters	Ref
Langmuir	$q_e = \frac{q_m K_L C_e}{1+K_L C_e}$	Type (I)$C_e/q_e = (1/K_L q_m) + (C_e/q_m)$	C_e/q_e vs. C_e	$q_m = (\text{slope})^{-1}$, $K_L = \text{slope/intercept}$	[36]
		Type (II)$1/q_e = (1/K_L q_m C_e) + (1/q_m)$	$1/q_e$ vs. $1/C_e$	$q_m = (\text{intercept})^{-1}$, $K_L = \text{intercept/slope}$	
		Type (III)$q_e = q_m - (1/K_L)(q_e/C_e)$	q_e vs. $1/C_e$	$q_m = \text{intercept}$, $K_L = -(\text{slope})^{-1}$	
		Type (IV)$q_e/C_e = K_L q_m + K_L q_e$	q_e/C_e vs. q_e	$q_m = -(\text{intercept/slope})$, $K_L = -(\text{slope})$	
		Type (V)$1/C_e = K_L q_m(1/q_e) + K_L$	$1/C_e$vs. $1/q_e$	$q_m = \text{slope/intercept}$, $K_L = -(\text{intercept})$	
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln q_e = \ln K_F + (1/n)\ln C_e$	$\ln q_e$vs. ln C_e	$K_F = \exp(\text{intercept})$, $n = (slope)^{-1}$	[37]
Temkin	$q_e = q_m \ln(K_T C_e)$	$q_e = q_m \ln K_T + q_m \ln C_e$	$q_e$vs. $\ln C_e$	$K_F = \exp(\text{intercept/slope})$, $q_m = \text{slope}$	[38]

Table 3
Isotherms parameters, correlation coefficients value and ARE

Soils	SA	SE	SA	SE	SA	SE
Isotherms	R^2		ARE (%)		Parameters	
Langmuir						
Type (I)	0.99	0.99	2.92	3.45	q_m = 3.99; K_L = 0.36	q_m = 3.82; K_L = 0.28
Type (II)	0.95	0.96	2.79	3.02	q_m = 3.96; K_L = 0.36	q_m = 3.98; K_L = 0.21
Type (III)	0.89	0.96	20.24	22.6	q_m = 3.86; K_L = 0.14	q_m = 3.79; K_L = 0.1
Type (IV)	0.91	0.92	3.36	3	q_m = 4.05; K_L = 0.32	q_m = 4; K_L = 0.21
Type (V)	0.95	0.96	3.07	3	q_m = 4; K_L = 0.34	q_m = 4.02; K_L = 0.20
Freundlich	0.90	0.84	153.6	5.91	K_F = 2.04; n = 6.06	K_F = 1.78; n = 5.42
Temkin	0.90	0.87	35.33	30.03	q_m = 0.52; K_T = 3.41	q_m = 0.55; K_T = 2.66

In this case, adsorption process was judged by the correlation coefficients, R^2 values. So Langmuir-type (I) isotherm model of the SA and SE samples was fitted better than the other isotherm models. The adsorption isotherm models were fitted to the experimental data for SA sample in the order of: Langmuir type (I) > Langmuir type (II&V) > Langmuir type (IV) > Temkin > Freundlich > Langmuir type (III) isotherm. In SE sample, the isotherm models were fitted to the data as follows: Langmuir type (I) > Langmuir type (II&V) > Langmuir type (III) Langmuir type (IV) > Temkin > Freundlich isotherm.

The Cu (II) adsorption isotherms are similar to L-curves (Fig. 2(a) and (b)). In the L-shaped isotherm, the ratio between the concentration of Cu (II) remaining in solution and adsorbed on adsorbent decreases when Cu (II) concentration increases [39]. This trend can be due to decrease in vacant adsorption sites resulted from covering by adsorbate [12]. It can be implied that the soil particles have higher affinity to adsorb metals ions at low concentration and show a reducing tendency as the concentration of adsorbed metals reaches the maximum adsorption capacity of the soil [40].

Distribution coefficients (K_d) represent the affinity of the metal retention in soil vs. solution. In fact, the mobility and fate of metals can be estimated by K_d values in soil [41]. High values of K_d indicate that the metal tends to retain in the solid phase through adsorption reactions and low values indicate that an important proportion remains soluble [42]. The value of K_d was calculated at varying initial Cu (II) concentrations in Table 4. Range of Cu–K_d values were obtained for SA and SE (0.6–5.3) and (0.5–3.4), respectively. SA samples showed higher K_d values against SE samples which this indicates SA has higher potential for Cu (II) adsorption than SE. The K_d was extremely dependent on the initial metal

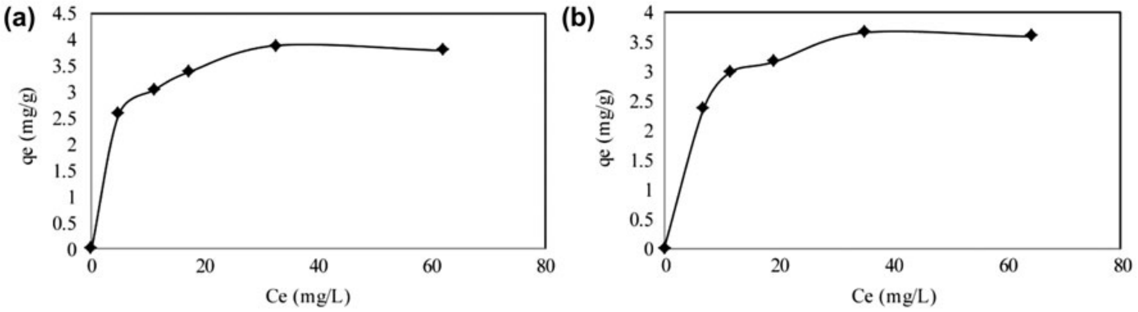

Fig. 2. Cu (II) adsorption isotherms (a) for SA and (b) SE sample.

Table 4
K_d values were calculated for SA and SE samples

Soil	SA					SE				
Cu concentration	30	40	50	70	100	30	40	50	70	100
K_d	5.31	2.73	1.97	1.18	0.6	3.41	2.56	1.63	1.04	0.55

concentration so that with increase in initial Cu (II) concentration from 30 to 100 mg/L, K_d values decreased for both SA and SE. This proves that the adsorption capacity of soil decreases in high Cu (II) concentrations. SE shows a lower organic matter and $CaCO_3$ contents than SA and hence a reduced adsorption capacity can be due to the lower presence of sorbing phases such as carbonate contents and organic matter. These results are similar to those obtained by Sastre and et al. [43]. On the contrary, the high K_d values in SA were expected which can be attributed to the high carbonates contents.

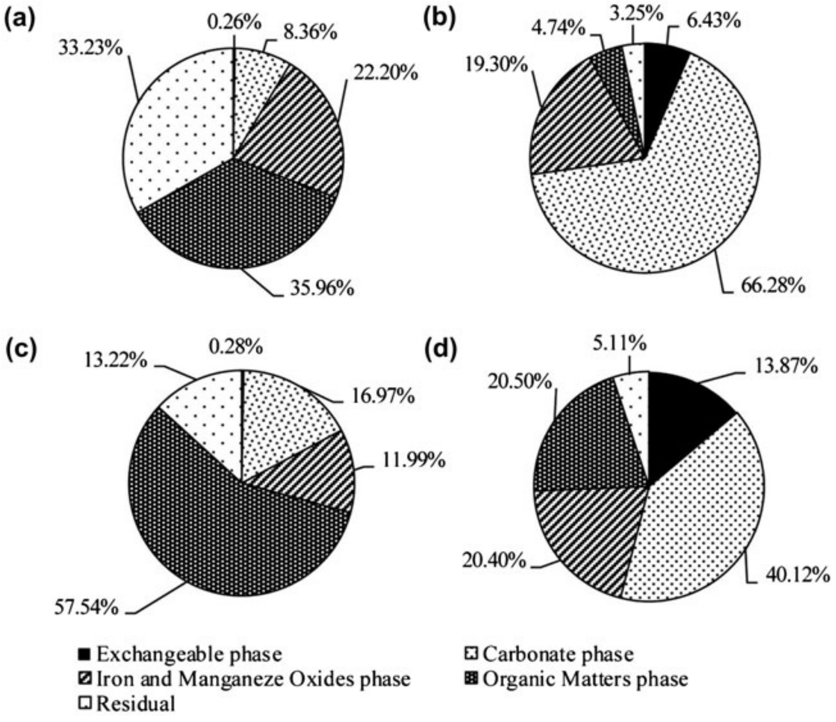

Fig. 3. Sequential extraction results (a) for SA before and (b) after adsorption (c) for SE before and (d) after adsorption.

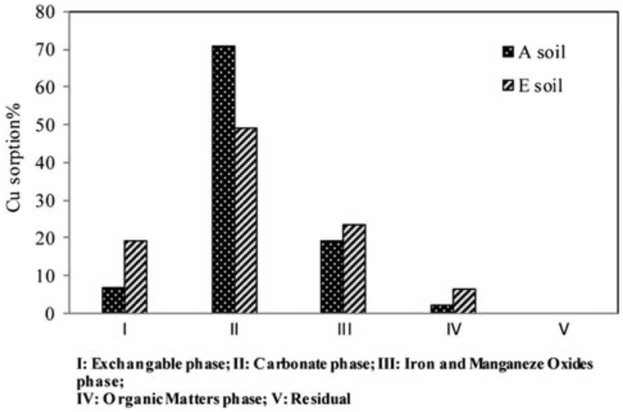

Fig. 4. The percentage of Cu (II) adsorption onto various fractions of SA and SE.

3.2. Sequential extraction

Sequential extraction was conducted for the assessment of the main sorbents of metal ions in soils [44]. The total amount of heavy metals in various fractions of soil can be determined using this method. The percentage fractionation of copper in SA before and after adsorption (Fig. 3(a) and (b)) follows the order: Organic matter > residual > Iron and Manganese Oxides > carbonates > exchangeable, and carbonate > Iron and Manganese Oxides > exchangeable > Organic matter > residual, respectively. After adsorption, 66% of Cu (II) sorbed is associated with carbonate phase. Results indicate that carbonate phase for Cu (II) adsorption in this soil is of prominent importance and after that iron and manganese oxides play an effective role in adsorption process.

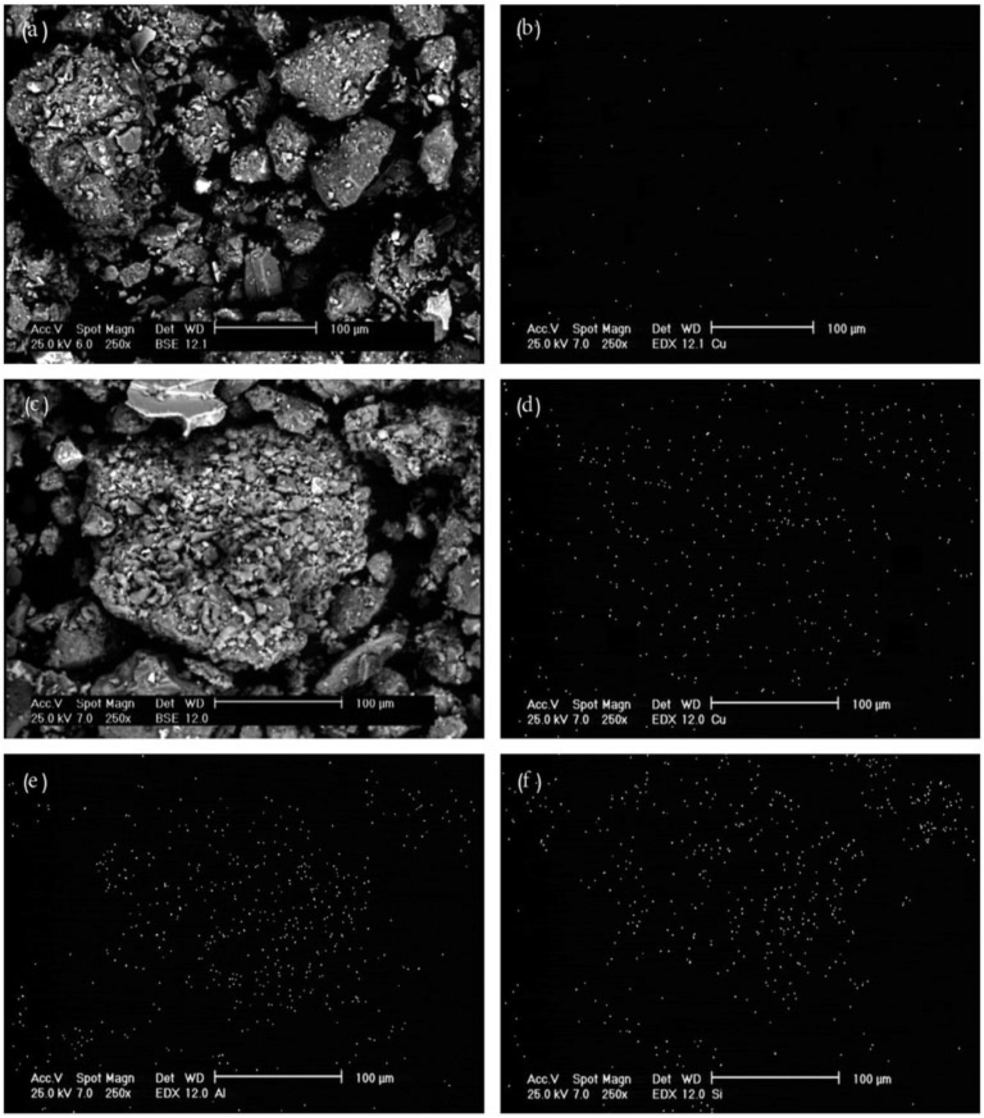

Fig. 5. (a)–(c) SEM photographs of the surface of SA sample before and after Cu (II) adsorption, respectively; (b)–(d) dispersion maps of Cu (II) before and after adsorption; (e)–(f) the distribution maps of Al and Si after adsorption.

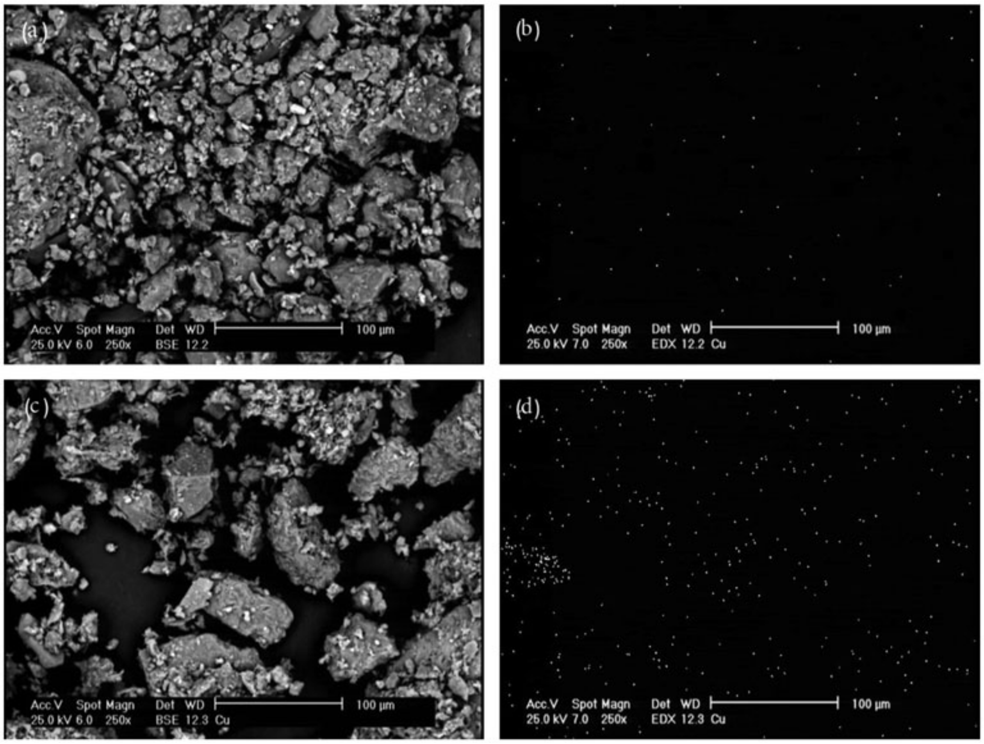

Fig. 6. (a)–(c) SEM photographs of the surface of SE sample before and after Cu (II) adsorption, respectively; (b)–(d) distribution maps of Cu (II) before and after adsorption, respectively.

Before adsorption process, the percentage of distribution Cu (II) into SE fractions was in order of: Organic matter > carbonates > residual > Iron and Manganese Oxides > exchangeable (Fig. 3(c) and (d)). The highest percentage of Cu (II) was associated with carbonates after adsorption mechanism. The highest amount of Cu (II) was sorbed onto SE by carbonate phase and then iron and manganese oxides, exchangeable phase and organic matter retained Cu, respectively.

The adsorption percentage of Cu (II) onto different fractions of SA in comparison SE is shown in Fig. 4. As it can be found, Cu (II) percentage sorbed by carbonate phase of SA is 71%, which is around 21% higher than that of adsorbed by carbonate phase in SE sample. On the other hand, the other phases such as exchangeable, iron and manganese oxides and organic matters in SE adsorb more amounts of Cu (II) in relative to SA. What the findings confirm is that the percentage of Cu (II) sorbed by total components of SA is more than that of SE.

3.3. SEM results

Fig. 5(a)–(c) shows the surface morphology of SA sample prior to and after adsorption, respectively. The distribution map and relative proportion of Cu (II) over the scanned area can be observed before adsorption (Fig. 5(b)). Fig. 5(d)–(f) shows the dispersion maps of Cu, Al, and Si, respectively. It can be seen that the SA sample has a negligible Cu (II) content before adsorption (Fig. 5(b)). Significant amounts of Cu (II) ions are detected over the scanned area after adsorption in Fig. 5(d). The correlation between Al and Si distribution may indicate the existence of clay minerals (Fig. 5(e) and (f)). It can be perceived that there is a relationship between distribution of Cu, Al, and Si. It can be found that Cu (II) ions are adsorbed on the surface of clay minerals in SA soil. The results of SEM confirm the findings of sequential extraction process. Exchangeable phases that involve clay minerals have an effective role in Cu (II) adsorption.

The surface morphology of SE sample is shown prior to and after adsorption in Fig. 6(a)–(c). Dispersion of Cu (II) on surface of SE sample increase after adsorption compared with before adsorption as it is shown in Fig. 6(b)–(d).

4. Conclusion

This study provides an opportunity to understand the role of different fractions of soils (such as exchangeable, carbonates, iron and manganese oxides and organic matter) surrounding SCM in Cu (II) adsorption. In addition, the adsorption capacity of these soil samples was investigated by isotherm models. For SA, the Langmuir type (I) isotherm model matched the equilibrium data better than the other isotherm models, revealing that the adsorption of Cu (II) onto SA was as monolayer adsorption. Also, these results were similar to those obtained for SE. K_d values of SA were high in comparison to those of SE that show SA sample has higher potential of Cu (II) adsorption than SE. The results of sequential extraction indicate that carbonate phase in SA and SE samples play a major role in adsorption of Cu (II) metal. Fe and Mn oxides were less effective in Cu (II) adsorption in SA relative to carbonates. In SE, Fe, and Mn oxides and exchangeable phase have significant impact in Cu (II) adsorption. According to the results of SEM, clay minerals in soil samples had remarkable role in Cu (II) adsorption.

Nomenclature

K_L — Langmuir isotherm constant (L/mg)
K_F — Freundlich constant (mg/g) $(L/g)^{1/n}$
$1/n$ — Freundlich exponent
K_T — Temkin isotherm constant (L/mg)
R^2 — correlation coefficient
ARE — average relative error
N — number of experimental measurements
C_e — equilibrium concentration (mg/L)
C_0 — initial concentration (mg/L)
q_e — amount of Cu (II) adsorbed at equilibrium (mg/g)
q_m — monolayer sorption capacity (mg/g)
V — volume of the solution (L)
W — mass of soil (g)

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