Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption from aqueous solutions by pyrite and synthetic iron sulphide

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Abstract

In this study, removal of Cu^{2+}, Cd^{2+} and Pb^{2+} from aqueous solutions by adsorption onto pyrite and synthetic iron sulphide (SIS) was investigated as a function of pH, contact time, adsorbent dosage, initial metal concentration and temperature. It has been determined that the adsorption of metal ions onto both adsorbents is pH dependent and the adsorption capacities increase with the increasing temperature. The mechanisms governing the metal removal processes were determined as chemical precipitation at low pH (<3) due to H$_2$S generation and adsorption at high pH (in the range of 3–6). The metal adsorption yields also increased with the increasing adsorbent dosage and contact time and reached to equilibrium for both adsorbents. The Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption capacities of both adsorbents decrease in the order of Pb^{2+} > Cu^{2+} > Cd^{2+}. Except for cadmium, little fraction of copper and lead in the solid adsorption residues was desorbed in acidic media.
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Keywords: Heavy metal; Chemical precipitation; Adsorption; Desorption; Pyrite; Iron sulphide

1. Introduction

Heavy metals and their compounds are widely used in different industrial applications such as metallurgy, chemistry, battery, paper and paint manufacturing. Increase in their usage has resulted in an increase in their amounts in the aquatic systems. Heavy metals are among the most important pollutants in waters. They are non-degradable and therefore continue to accumulate in water bodies [1]. Because of their toxic properties and the tendency for bio-accumulation in the food chain, it is imperative to take effective precautions and to reduce the concentration levels of heavy metals in waters.

There are various heavy metal treatment methods such as chemical precipitation, ion exchange, membrane systems, cementation and adsorption [2–4]. Among these methods, although the precipitation is a simple, easily automated and widely applied process, usually it is not effective to reduce heavy metal concentration to low level required by water quality standards [5]. Therefore, adsorption offers to the treatment of wastewaters containing moderate and low concentrations of metals. In the adsorption process, activated carbon has been the standard adsorbent. Due to its high-cost, production of its low-cost alternatives has been the focus of research in this area for years. For this purpose, the use of industrial and metallurgical wastes and by-products, biological wastes, natural substances and minerals have been studied as adsorbents for the wastewater treatment [6,7]. Several natural substances or metallurgical wastes were used as adsorbents for heavy metals uptake from water and wastewater including kaolin [8], kaolinite [9,10], perlite [11], montmorillonite and goethite [12–14], bentonite [15], iron oxides [16,17], dolomite [18], amorphous hydrous manganese dioxide [19], siderite [20], siderite/limestone [21], activated alumina [22], bauxite [23,24], fly ash [25,26], sand, silica and alumina [27], steel converter slag [28], blast furnace slag [29]. Pyrite has been evaluated for adsorption of molybdate and tetrathiomolybdate [30]. However, pyrite and synthetic iron sulphide have not been systematically investigated and evaluated for the metal adsorption purposes.

The aim of this paper is to investigate the effects of pH, adsorbent dosage, contact time, initial metal concentration and temperature on the Cu^{2+}, Cd^{2+} and Pb^{2+} removal from aqueous solution by pyrite and synthetic iron sulphide and to compare

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pyrite and synthetic iron sulphide with respect to their ability to remove Cu^{2+}, Cd^{2+} and Pb^{2+} ions from aqueous solution.

2. Materials and methods

2.1. Materials

The pyrite sample, collected from pyrite-bed, Keban-Elazığ (Turkey), and synthetic iron sulphide (SIS), catalogue number of which is Merck-3908, were used as adsorbents in this study. The samples in gross particles (pyrite) and pellets (SIS) were crushed separately. The visible impurities were removed by hand from pyrite sample and then the samples were ground and sieved. The fractionated materials in the particle size of <53 μm were dried at 60 °C for 6 h, and then they were stored in a tightly closed jar throughout the study.

In order to prepare the experimental solutions, stock solutions of Cu^{2+}, Cd^{2+}, Pb^{2+} (10 g/l) were prepared by dissolving their nitrate salts in distilled water. The working solutions were prepared by diluting these solutions with distilled water. Taking into consideration common concentration values of related metals in actual wastewaters [2,31], 100 mg-metal ion/l has been selected as the suitable initial metal concentration value. pH adjustments were made by using HNO_3 and NaOH solutions in various concentrations. All the chemicals used in the study were of analytical reagent grade.

2.2. Adsorption studies

Adsorption experiments were carried out in the batch reactors (250 ml erlenmeyer) containing various amounts of adsorbent and 100 ml of metal solutions having different concentrations and pH. The batch reactors were shaken at 150 rpm by using an orbital flask shaker (Gallenkamp) for contact times ranging from 5 to 150 min. From the obtained results, optimum pH, adsorbent dosage and contact time were selected for further investigation.

At the end of the predetermined contact period, reaction mixtures were filtered and then the final pH of the filtrates was measured by a pH meter. The filtrates were acidified with 1 ml of HNO_3 solution to prevent the precipitation of metal ions and then they were analyzed for related metals.

2.3. Desorption study

Desorption behaviours of metals from solid adsorption residues were investigated depending on pH. For this purpose, a 100 ml solution with desired pH was combined with 5 g of adsorption residue in a 250 ml erlenmeyer. The mixtures were agitated at 18 rpm for 24 h. All of the experiments were carried out at 25 °C. In order to model acid rains, pHs of the solution used in desorption experiments were adjusted with the mixture of sulphuric acid and nitric acid solution in a weight ratio of H_2SO_4 to HNO_3 1.16:1, which resembles acid rains [32,33], and NaOH solution.

The experiments were performed in duplicate and mean values were taken into account.

Table 1
Chemical and mineralogical compositions of the pyrite

Constituents	w/w
Fe	41.45%
S	36.43%
Al	2.20%
Ca	3.58%
Mg	1.18%
Si	5.47%
Cu	3700 mg/kg
Co	300 mg/kg
Ni	200 mg/kg
Mn	700 mg/kg
Zn	350 mg/kg

Minerals	Formula
Pyrite	FeS_2
Quartz	SiO_2
Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Natrosilite	$Na_2Si_2O_5$
Brussite	$CaHPO_4 \cdot 2H_2O$
Chamosite	$(Fe, Al, Mg)_6(Si, Al)_4O_{10}(OH)_8$

2.4. Methods of analysis

The concentration of metals in the solutions was determined by ATI-Unicam 929 atomic absorption spectrophotometer using flame atomization technique. pH measurements were done by a pH meter (Orion SA720). Standard solutions were prepared by using analytical chemicals. All dilutions were made by distilled water.

Pyrite and SIS samples used in the study were subjected to wet chemical analysis [34,35]. Mineralogical composition of the adsorbents was determined by Siemens D-5000 model X-ray diffractometer.

3. Results and discussion

3.1. Chemical and mineralogical characterizations of pyrite and SIS

Chemical and mineralogical compositions of pyrite and SIS are presented in Tables 1 and 2. As seen, pyrite contains 41.45% Fe, 36.43% S, 5.47% Si, 3.58% Ca and 2.2% Al as major elements. Varying amounts of other minor elements such as Cu, Co, Ni, Mn and Zn also exist in the material.

Table 2
Chemical and mineralogical compositions of the SIS

Constituents	w/w (%)
Fe	61.03
S	32.82

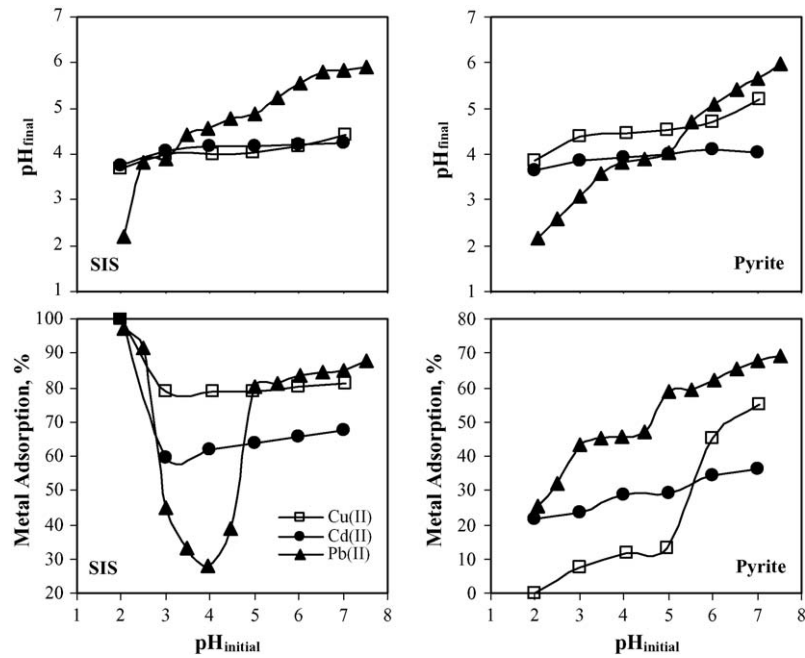| Minerals	Formula
Troilite	FeS
Iron	Fe
Wustite	FeO (minor amount)

Fig. 1. The effect of pH on the Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption by SIS and pyrite.

The pyrite and SIS contain 41.45% and 61.03% Fe and 36.43% and 32.82% S, respectively. As seen from the tables, iron is a constituent of the some other minerals except for pyrite and SIS. Therefore, by taking into account sulphur contents of the samples, it can be calculated that the pyrite and SIS contain 68.3% FeS_2 and 90.25% FeS in weight, respectively. The excessive iron amount of SIS sample with respect to stoichiometric sulphur is in the form of metallic iron. XRD patterns confirm this situation.

XRD analysis of the samples used show that the pyrite sample is composed mainly of pyrite and secondary of dolomite and quartz, SIS is composed mainly of troilite and secondary of metallic iron.
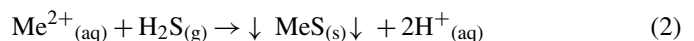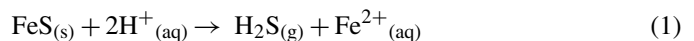
3.2. Removal study

3.2.1. Effect of pH

The effect of the pH on Cu^{2+}, Cd^{2+} and Pb^{2+} removal by either pyrite or SIS was investigated at the pH range of 2–7.5, temperature of 25 °C for contact time of 90 min. The results obtained are presented in Fig. 1.

In the studies carried out with SIS, it has been determined that the metal adsorption yields are high at the low pH and they decrease with the increasing pH up to 4 and then they increase at low rate again. When taking into account that metal ions have positive charge, it can be stated that the metal ions can be more effective adsorbed at the high pH values. On the contrary, the metal adsorption yields in the presence of SIS are rather high at pH below 3. This associated with H_2S generation in acidic media (Eq. (1)). H_2S is known as an efficient reagent for metal precipitation in the form of metal sulphides. Therefore, due to generation of H_2S in solutions having pH below 3, Cu^{2+}, Cd^{2+}

and Pb^{2+} precipitate as their sulphides (Eq. (2)) and consequently metal adsorption yields increase:

$$FeS_{(s)} + 2H^+_{(aq)} \rightarrow H_2S_{(g)} + Fe^{2+}_{(aq)} \tag{1}$$

$$Me^{2+}_{(aq)} + H_2S_{(g)} \rightarrow \downarrow MeS_{(s)}\downarrow + 2H^+_{(aq)} \tag{2}$$

where Me^{2+} is a metal ion (i.e. Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Fe^{2+}) which can precipitate as metal sulphide.

Although pyrite is also a sulphidic mineral, this increase at low pH values was not observed due to the presence of impurities such as calcite and dolomite in the pyritic sample which consumes acid before sulphur according to reaction depicted by Eq. (3):

$$CaCO_{3(s)} + 2H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)} \tag{3}$$
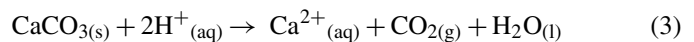
Based on the experimental results obtained using pyrite as an adsorbent (Fig. 1), it has been determined that the adsorption yields increase with pH. The plot of pH versus percentage lead removed on pyrite has two inflection points: one at pH 4.5, where significant adsorption of lead begins and the other at pH 6, where the removal increases. This increase in lead removal above pH 6 was probably due to the precipitation of lead ions as insoluble $Pb(OH)_2$ and not due to adsorption [36,37]. Therefore, it can be noted that the optimum pH for lead adsorption is 5. The same tendency has also been observed for copper adsorption onto pyrite. Copper adsorption increases drastically above pH 5. As Cu^{2+} precipitates above pH 6.5 in the form of $Cu(OH)_2$ [38], optimum pH for copper adsorption onto pyrite is 6.

The final pH of the solutions is also shown in Fig. 1. The values are below the precipitation pH values of the metal ions. Therefore, it can be stated that the mechanism governing the removal process may be adsorption.
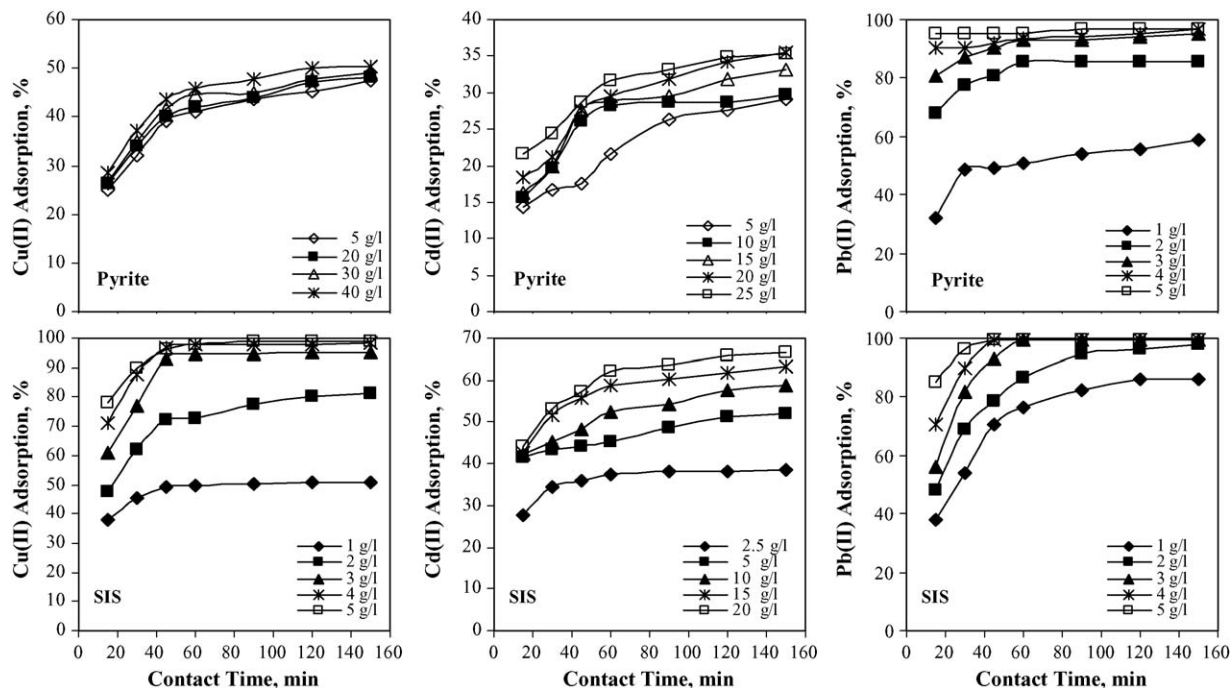
Fig. 2. The effects of adsorbent dosage and contact time on the Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption by pyrite and SIS.

Consequently, for both adsorbents, optimum pHs were selected to be 6 for Cu^{2+} and Cd^{2+} and 5 for Pb^{2+}.

3.2.2. Effects of adsorbent dosage and contact time

The effect of adsorbent dosage on the adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} was investigated for initial concentration of $100\ mg\text{-}Me^{2+}/l$ at pH optimized for each metal ion depending on contact time. The results are shown in Fig. 2.

The metal adsorption yields in all cases for both adsorbents increase with the increasing adsorbent dosages. However, in order to obtain same adsorption yields for metal ions having the concentration of 100 mg/l except for lead ions, pyrite dosage to be used must be higher than SIS. This difference can be explained with sulphur on the SIS surface. Sulphur on the SIS surface serves as an active center for related metal ions that are adsorbed from the solution by bounding these centers.

As seen Fig. 2, copper, cadmium and lead adsorption yields for pyrite dosages in the range of 5–40, 20–25 and 3–5 g/l are close to each other, respectively. Therefore, it can be noted that a further increase in pyrite dosage higher than 5, 20 and 3 g/l for copper, cadmium and lead ions has a negligible effect on the metal adsorption, respectively. Maximum metal adsorption yields for SIS were obtained in the SIS dosage of 5 g/l for copper, 20 g/l for cadmium and 3 g/l for lead.

The adsorption yields also increase with contact time and attain a maximum value at a certain contact times for each metal and each adsorbent dosage of both adsorbents, thereafter, they remain almost constant. At these points, the adsorbents surfaces are saturated with metal ions. While optimum contact times for pyrite adsorbent dosages of Cu^{2+}, Cd^{2+} and Pb^{2+} optimized were determined to be 120, 120 and 60 min, those for SIS were determined to be 45, 120 and 45 min, respectively.

On the contrary copper and cadmium adsorption, rather high and almost same lead adsorption yields with same pyrite and SIS dosages have been obtained. In order to research this difference between the related metals having same properties, some supplementary experiments were carried out. In these experiments, it was investigated that if the adsorbents used contain other removing components for lead. Pyrite and SIS are sulphide mineral. The sulphide, can be oxidized in the course of time and it converts to sulphate, is a precipitation reagent for lead ions. In this case, lead ions in the solution precipitate in the form of insoluble $PbSO_4$ (Eq. (4)). In order to determine sulphate contents of the adsorbents, 3 g of pyrite and SIS samples (optimum dosages) were taken and mixed with 1 l of distilled water and then shaken for 60 min. After filtration of mixture, sulphate amount of the each adsorbent was gravimetrically analyzed [35]. The results obtained showed that the SIS does not contain sulphate, however, the pyrite used contains sulphate ions that will precipitate 74% of lead ions in the solution. According to these results, it can be concluded that the lead uptake onto pyrite is governed with together adsorption and chemical precipitation:

$$Pb^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \rightarrow \downarrow PbSO_{4(s)} \tag{4}$$

3.2.3. Effect of initial metal concentration

The effect of initial metal concentration on the adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} was investigated under the conditions of pH, adsorbent dosage and contact time optimized for each metal and adsorbent. The metal adsorption percentages and calculated adsorption densities depending on the initial concentration are shown in Fig. 3. As expected, metal adsorption yields decrease by increasing initial metal concentration.
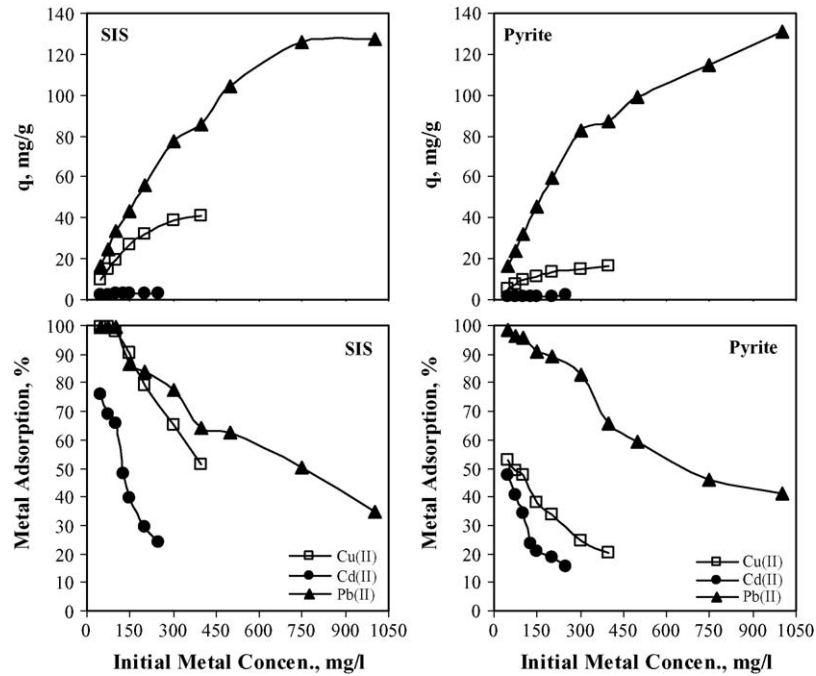
Fig. 3. The effect of initial metal concentration on the Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption by SIS and pyrite.

About 90% of Cd^{2+} and Pb^{2+} in the solutions having the concentration range of 50–150 mg/l can be removed by SIS. But, except for lead, adsorption yields in the presence of pyrite are quite low and amounts of the metal ions adsorbed per unit pyrite are almost constant. Depending on adsorption densities, metal adsorption capacities of both adsorbents decrease in the order of $Pb^{2+} > Cu^{2+} > Cd^{2+}$. These results are agree with the results obtained from adsorption studies of some bivalent heavy metal ions from aqueous solutions by manganese nodule leached residues [39] and humic umbrisols [40].

3.2.4. Effect of temperature

The effect of temperature on the Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption was investigated at 25, 35 and 45 °C and under the optimized conditions for each metals and adsorbents. The adsorption data at different temperatures indicated that there are significant changes in the metal adsorption. When the temperature of solution is raised from 25 to 35 °C, the Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption yields onto SIS increase from 96.3%, 53.3% and 81.7% to 99%, 78.8% and 88.2% at the end of contact period of 30 min, respectively. The contact times required to reach equi-
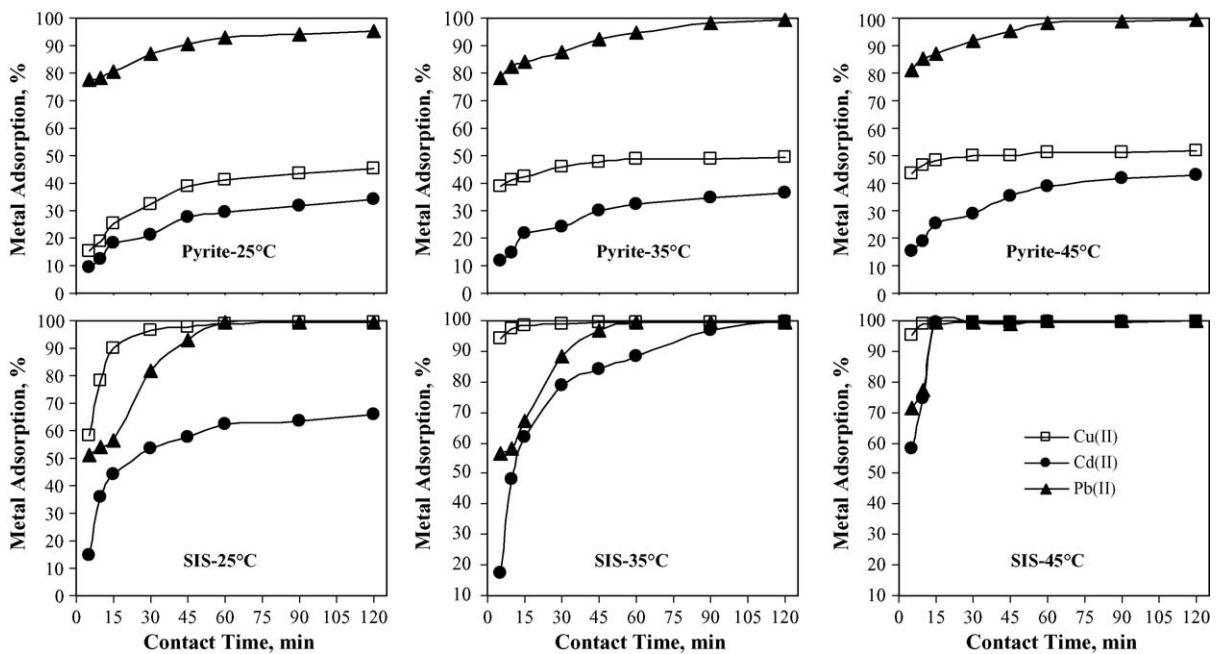

Fig. 4. The effect of temperature on the Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption by pyrite and SIS.

Table 3
Results of the desorption experiments applied to the solid adsorption residues

pH	SR1[a], concentrations of desorbed metals (mg/l)			SR2[b], concentrations of desorbed metals (mg/l)		
	Pb	Cu	Cd	Pb	Cu	Cd
2	0.59	1.92	3.40	1.76	1.73	1.20
3	8.24	5.88	6.60	1.76	ND[c]	UDL[d]
4	6.41	5.55	6.20	1.4	ND[c]	UDL[d]
5	5.83	4.85	6.40	1.1	ND[c]	UDL[d]
6	3.78	2.03	2.32	1.1	ND[c]	UDL[d]
7	1.98	1.79	2.30	1.1	ND[c]	UDL[d]
8	1.74	1.10	2.18	1.1	ND[c]	UDL[d]
9	1.74	1.20	2.06	1.1	ND[c]	UDL[d]

Liquid/solid: 20; temperature: 25 °C; contact time: 18 ± 2 h.

[a] SR1: solid residue of adsorption process that SIS was used as an adsorbent.

[b] SR2: solid residue of adsorption process that pyrite was used as an adsorbent.

[c] ND: not detected.

[d] UDL: under the detection limit.

librium is also shorten. Each raise of 10 °C in the temperature shortens the equilibrium time required about 15 min. Increasing in the metal adsorption yields with increasing temperature was also observed for pyrite (Fig. 4). Similar results were found by Panday et al. who have investigated copper adsorption onto fly ash [41]. In addition, Erdem and Özverdi have reported that the adsorption yield of lead onto siderite increases with the increasing temperature [20].

Consequently, it can be concluded that the adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} onto pyrite and SIS are endothermic. In addition, the increases in metal adsorption by the increasing temperature suggest that the mechanism governing the adsorption process may be chemical.

3.3. Desorption study

As seen from the figures given in Table 3, the concentrations of desorbed metals were varied with pH and type of the residue. The concentration of metals desorbed from solid residue (SR1) of adsorption process that SIS was used as an adsorbent were higher than those of the solid residue (SR2) of adsorption process that pyrite was used. Maximum desorption from SR1 was observed at pH range of 3–6. At this range, maximum concentrations of lead, copper and cadmium dissolved were found to be about 8.24, 5.88 and 6.6 mg/l, respectively. These concentration values correspond 4.94, 5.88 and 38.54% of metals in SR1. Over pH 6, the values were close each other. While copper and cadmium was only desorbed in the concentration of 1.73 and 1.2 mg/l from SR2 at pH 2, respectively, lead was desorbed at all pH investigated. But, its concentration was not change at pHs over 4. It has been determined that the 1.09% of lead, 3.83% of copper and 20% of cadmium in SR2 were dissolved at pH 2.

When the metal concentration values desorbed from both residues are compared, it can be concluded that the SR2 is environmentally more stable than the SR1. This result is an advantage for usage of the cheapest and abundant pyrite mineral for this purpose.

4. Conclusions

The following conclusions can be drawn from this study in which pyrite and synthetic iron sulphide (SIS) were used as adsorbent for Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption from aqueous solution.

Adsorptions of Cu^{2+}, Cd^{2+} and Pb^{2+} onto both adsorbents are pH and temperature dependent. For the solution of 100 mg-Me^{2+}/l, the maximum adsorption yields in the presence of pyrite at 25 °C were found as 45.2% at the conditions of adsorbent dosage: 5 g/l, pH 6, contact time: 120 min for Cu^{2+}, 34.2% at the conditions of adsorbent dosage: 20 g/l, pH 6, contact time: 120 min for Cd^{2+} and 94.2% at the conditions of adsorbent dosage: 3 g/l, pH: 5, contact time: 60 min for Pb^{2+}.

In the case of SIS, the maximum adsorption yields for the solution of 100 mg-Me^{2+}/l were determined as 99.1% at the conditions of adsorbent dosage: 5 g/l, pH 6, contact time: 45 min for Cu^{2+}, 68.5% at the conditions of adsorbent dosage: 20 g/l, pH 6, contact time: 120 min for Cd^{2+} and 99.8% at the conditions of adsorbent dosage: 3 g/l, pH: 5, contact time: 45 min for Pb^{2+}.

The metal adsorption yields increase with the increasing temperature and decreasing initial metal concentration. That the adsorption capacities increase with an increase in temperature shows that the adsorption process is endothermic. The Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption capacities of both adsorbents decrease in the order of $Pb^{2+} > Cu^{2+} > Cd^{2+}$.

The desorption studies indicated that the concentration of metals desorbed from solid residue (SR1) of adsorption process that SIS was used as an adsorbent were higher than those of the solid residue (SR2) of adsorption process that pyrite was used. However, except for cadmium, little fraction of copper and lead in the solid adsorption residues was desorbed in acidic media.

Taking into consideration present findings, the both adsorbents seem to be good adsorbents for copper, cadmium and lead ions. But, sulphide of these materials can convert to sulphate under the environmental conditions. This conversion is a disadvantage for metal ions whose sulphate compounds have high

solubility. Among the metal ions investigated, sulphate salts of copper and cadmium can easily dissolve in water. When the adsorption residues of these metals are discharged in landfill, the metals can release. However, lead sulphate, has quite a low solubility product, cannot dissolve in water. The fact that the sulphide of the mineral convert to sulphate in the course of time causes formation of more stable purification residue such as lead sulphate. Therefore, the both adsorbents for lead are more appropriate than the other metals. Particularly, since pyrite is one of the abundant minerals and it is also a by-product of copper production, it can be concluded that the pyrite is a lower-cost adsorbent for lead adsorption.

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