**Desalination and Water Treatment**
www.deswater.com

21 (2010) 335–345
September

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doi: 10.5004/dwt.2010.1412

# The effect of Si and Fe impurities on the removal of $Cu^{2+}$ and $Co^{2+}$ from Co/Cu aqueous solutions using natural clinoptilolite as an ion-exchanger

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Received 13 December 2009; accepted 24 March 2010

## ABSTRACT

In this study, the impact of Si and Fe impurities on the removal of $Cu^{2+}$ and $Co^{2+}$ from aqueous solutions was investigated using Southern African clinoptilolite as an ion-exchanger in a multi-component system. The extent of the cation-exchange process was investigated, whereby mixed Co/Cu aqueous solutions of concentrations 0.0020 M, 0.0698 M and 0.2000 M of $Co^{2+}$ and $Cu^{2+}$ were analyzed using atomic absorption spectroscopy (AAS). These Co/Cu mixed solutions were used as ''control'' solutions in determining the impact of the presence of impurities such as $SiO_2$ and $FeCl_2$ in mixed Co/Cu aqueous solutions on the removal efficiencies of copper and cobalt from the solutions. It was found that both $SiO_2$ and $FeCl_2$ greatly reduced the removal efficiency of $Cu^{2+}$, especially where there were high amounts of $SiO_2$ in the Co/Cu solution. There was however a significant enhancement in the removal efficiency of $Co^{2+}$ with increased concentration of $SiO_2$.

***Keywords:*** Clinoptilolite; Ion-exchange; Copper; Cobalt; Si/Fe impurities

## 1. Introduction

Aqueous solutions emanating from metallurgical operations and electroplating industries have been highlighted as avenues through which surface water and groundwater can be polluted [1]. Metallurgical plants are generally located in sparsely inhabited areas near the mines and until recently ecological challenges, such as acid mine drainage, due the location of the mines had not been seriously considered. However, with the accumulated knowledge on the influence of heavy metals on environmental pollution and growing public apprehension, the reduction of pollutants from metallurgical plants is of utmost importance to modern industries [2]. In mineral processing, another metal besides the targeted metal that is present in the leach liquor (aqueous solution) is loosely referred to as an ''impurity''. The major impurities that are associated with the processing of copper and cobalt are Fe, Si, Mn, Se and Mg and their concentration levels differ with each type of mineral ore [3].

While a number of water purification methods are currently employed in the drinking water industry, industrial wastewaters often contain other chemical impurities such as $SiO_2$ and $FeCl_2$ that may impose high cost implications for their removal from aqueous solutions during water treatment. The limitations of conventional methods in metal removal from aqueous solutions in multi-component systems (solutions that bear more than one ionic species) are still a subject of research. The concentration of these impurities in aqueous solutions largely influences the removal of

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Table 1
Characteristics of clinoptilolite [9,10]

| Feature | Description |
|---|---|
| Chemical formula | $Na_{0.1}$ $K_{8.57}$ $Ba_{0.04}$ $(Al_{9.31}$ $Si_{26.83}$ $O_{72})\cdot$ $19.56H_2O$ |
| Color | colourless, white, pink, yellow, reddish and pale brown |
| Lustre | Vitreous to pearly on the most prominent pinacoid face and on cleavage surfaces. |
| Transparency | Crystals are transparent to translucent |
| Crystal Habits | include blocky or tabular crystals with good monoclinic crystal form |
| Structure | Have a framework of alumino-silicates based on an infinite 3D-structure of $SiO_4$ and $AlO_4$ tetrahedral molecules linked by a shared oxygen atom. Variable Si/Al ratios and exchangeable ions e.g. $Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$. |
| How they are formed | Mostly formed by the alteration of glass-rich volcanic rocks with fresh water in playa lakes or near seawaters |
| Other Characteristics | Can absorb a high amount of water after drying and retain its structure even after heating to very high temperatures. |

targeted metals from such solutions. The relationship between an ion-exchanger's selectivity and the concentration of the aqueous solution containing the metal to be removed has been previously reported [4,5,6]. The initial ion concentration was found to be crucial in determining the kinetics for the adsorption of metals to a specific adsorbent at different metal and ionic ''impurity'' concentrations. Some studies have revealed that the metal loading amounts of ions increases as the initial ion concentration increases [7]. Therefore, in order to compare the influence of different ionic species present in solution on metal removal efficiency, the concentration ratios of these ionic components should be varied while keeping constant other experimental parameters of the system. The system that was investigated in this study involved the use of the natural clinoptilolite, a zeolite, as an ion exchanger.

Zeolites are crystalline, naturally occurring hydrated alumino-silicate minerals of alkali and alkaline earth cations which can be used in water treatment as ion-exchangers. In practice, both synthetic and natural zeolites are used for pollution control [8]. With the elucidation of their structural properties, zeolites have been exploited in industrial, agricultural, and biological industries for many years and recently they have been applied in environmental mitigation technologies [8]. Characteristic features of clinoptilolite are summarized in Table 1 [9,10]. Purity and mineralogical characteristics of clinoptilolite may vary to a large extent from one deposit to another [11]. Essentially, a number of characterization methods for zeolites have been reported for mineralogical studies and these include X-ray diffraction (XRD), X-ray fluorescence (XRF), Scanning Electron Microscopy (SEM/EDS) and other classical zeolite analyses techniques [11].

Clinoptilolite is the most abundant and cosmopolitan natural zeolite and has been specifically exploited for its ion-exchange capabilities since its interstitial cations can be exchanged with external cations in solution [12]. Natural zeolites, such as clinoptilolite, are capable of losing and gaining water in a reversible manner while exchanging their extra framework cations without altering the crystalline structure of the zeolite [12]. The ion-exchange process in zeolites is made possible by the presence of extra-framework cations which are located in a regular array of channels and cages that constitute the rigid anionic framework. Cations which normally fill the zeolite microspores are bound to the lattice and water molecules [13]. When the zeolite comes into contact with an electrolytic solution, the exchangeable cations of the zeolite can be removed from their sites and replaced by ions in the solution with which the zeolite has interacted.

Effective removal of $Cu^{2+}$ and $Co^{2+}$ by clinoptilolite has been reported from studies of solutions of a single and multi-component nature. Some of the studies reported the order of clinoptilolite's selectivity of $Cu^{2+}$ and $Co^{2+}$ in multi-component systems to be $Cu^{2+} > Co^{2+}$ [14,15]. On the other hand, Erdem et al. [16] reported that clinoptilolite selects $Co^{2+}$ over $Cu^{2+}$. In this study it was found that in a multi-component system Southern African clinoptilolite was more selective of $Co^{2+}$ over $Cu^{2+}$. However, in another study it was found that clinoptilolite was highly selective of $Cu^{2+}$ in single cation solutions of $Cu^{2+}$ and $Co^{2+}$ [17]. The difference in selectivities may be due to the geographical location of the clinoptilolite that was used or the composition of the multi-component system under study. In Table 2, natural clinoptilolite is compared to other adsorbents in removing some heavy metals from solution.

Table 2
Adsorption capacities (mg/g) of different adsobents for $Cu^{2+}$, $Co^{2+}$ and $Zn^{2+}$.

| Material | $Cu^{2+}$ | $Co^{2+}$ | $Zn^{2+}$ | Reference |
|---|---|---|---|---|
| Clinoptilolite | 1.64 | 1.42 | | [30,31] |
| | 3.70 | 1.50 | | |
| Fly-ash | 1.39 | | | [32] |
| Fly-ash wollastonite | 1.18 | | | [33] |
| Eutrophic peat | 12.07 | | 11.2 | [34,35] |
| | 19.56 | | | |
| Oligotrophic peat | 12.07 | | 13.08 | [34,35] |
| | 6.41 | | | |
| chabazite | 5.1 | 5.8 | 5.50 | [31] |
| chitosan | 222 | | | [36, Huang et al. 1996] |
| | 16.8 | | | |

Some data obtained on the behavior of the so-called multi-component systems clearly demonstrate that the removal efficiency of metal ions is greatly affected by the presence of competitive cations [18]. Interactions between metal ions and complexing ligands is an important factor which may fall into three categories based on the origin and the strength of the interactions: (i) Metal-ligand complexes may form in solution (ion-pairing) and weakly adsorb on the exchanger's surface or not form at all. In this case the formation of soluble complexes may compete with reactions which form ''surface complexes'' resulting in a reduction of the ion-exchange capabilities compared to a system that forms no complexing ligands. (ii) The competitive ions may interact indirectly at the surface of the ion-exchanger by altering the surface electrical properties of the ion-exchanger. For instance, the ions may adsorb on the clinoptilolite and make the surface more favorable for a particular metal ion present in the solution. (iii) The metal-ligand complex may adsorb strongly on the surface of the ion-exchanger in order to enhance the removal of the targeted metal ion, the competitor or both from aqueous solutions [19].

Studies reported elsewhere have documented the behaviour of multi-component systems using natural zeolites from different geographical locations across the globe [20,21]. However, the impact of Si/Fe impurities in the removal of either cobalt or copper from aqueous solutions using Southern African clinoptilolite has not been previously reported. While metal removal methods for water purification processes are known, aqueous solutions resulting from metallurgical operations, being multi-component in nature, require marginal cost effective methods for metal removal or recovery. It is therefore essential to investigate the behaviour of solutions in a multi-component system and further develop a metal removal strategy that is simple and affordable, hence the use of natural clinoptilolite. Herein, we determine the effect of the presence of Si/Fe impurities in an aqueous solution on the removal of $Co^{2+}$ and $Cu^{2+}$ using a natural clinoptilolite obtained from the Southern African region.

## 2. Experimental procedures

### 2.1. Chemical reagents and materials

All chemicals used in this research were of analytical reagent grade and were obtained from Sigma Aldrich and Merck. The clinoptilolite used was supplied by Prattely South Africa which had been sourced from the Vulture Creek, KwaZulu-Natal Province of South Africa.

### 2.2. Experimental techniques

Characterisation and mineralogical studies of the clinoptilolite were done using XRD and XRF. Surface appearance of the clinoptilolite was examined using SEM whereas for surface area and pore volume determination of the clinoptilolite the BET method was used. Chemical conditioning of the zeolite was monitored using FTIR spectroscopy while the thermal stability of the zeolite was analyzed using TGA. All metal ion content analyses were performed using atomic absorption spectroscopy (AAS) [17].

### 2.3. Conditioning of clinoptilolite

In addition to original forms, conditioned forms of clinoptilolite were also used in this study. Conditioning of the samples aimed at enhancing the ion exchange capacity of the zeolite by replacing exchangeable cations on clinoptilolite structure with a single cation. Hydrochloric acid (HCl) was selected as the conditioning agent since $H^{+}$ ion is weakly bound to the clinoptilolite and once the clinoptilolite is converted to the homoionic form, the $H^{+}$ can easily exchange with heavy metal cations [22]. The raw zeolite was crushed with jaw crushers and sieved through screens to a particle size range of 2.8–5.6 mm. The average particle size fractions was rinsed with distilled water and air-dried for 24 h. Chemical conditioning of clinoptilolite was performed using a HCl acid solution whose concentration was 0.02 M. Fractions of the clinoptilolite were soaked in the respective solution for 8 h, rinsed three times in deionised water of pH 6.7 and oven-dried at 50°C for 24 h. These optimum conditions used for the preparation of the conditioned clinoptilolite were based on preliminary experiments performed at different concentrations of HCl.

## 2.4. Analysis techniques

### 2.4.1. Atomic absorption spectroscopy (AAS) analysis

Atomic absorption spectroscopy was used to determine the concentration of $Cu^{2+}$ and $Co^{2+}$ in the solutions before and after the column sorption experiments which are described in detail in Section 2.5.3. These were done to determine the performance of the zeolite in recovering the targeted metals. Standards of 1,000 (mg/L), 2,000 (mg/L) 3,000 (mg/L) solutions were prepared and a calibration curve was drawn using these standards. Dilution was applied stoichiometrically where the concentrations of unknown solutions of $Co^{2+}$ and $Cu^{2+}$ exceeded the standards' concentration range. The solutions were analysed for final metal content using AAS in order to ascertain the zeolite's removal/recovery efficiency. The flame type used for AAS analyses was air-acetylene and the adsorption wavelengths used were: Cu (324.7 nm), Co (240.7 nm) and a spectral band of 0.2 nm for both metals in all AAS analyses.

## 2.5. Adsorption

For the sorption studies, the amount of metal sorption was computed as follows:

$$\% \text{ metal sorption by clinoptilolite} = \frac{C_i - C_f}{C_i} \times 100, \tag{1}$$

where $C_i$ is the initial solution concentration, $C_f$ is the final solution concentration.

## 2.6. Sorption process

Sorption testing experiments were conducted to verify the nature of the sorption mechanism. Initially, an exact mass (25 g) of the dried original clinoptilolite was brought into contact with a 25 mL of an aqueous solution containing either cobalt or copper ions. The initial concentrations of $Cu^{2+}$ and $Co^{2+}$ were 0.0020 M, 0.0698 M and 0.2000 M. Blank solutions containing no zeolites were also used. The concentration of the remaining metal ions was analysed with AAS. These concentrations were compared with the initial concentrations. After noting the initial and final concentrations of the aqueous solutions, it was evident that indeed metal adsorption had taken place since the final concentration was lower than the initial concentration.

## 2.7. Synthetic solutions preparation

The possible influence of one cation on the other's ($Co^{2+}$ or $Cu^{2+}$) removal efficiency were studied by variation of the metal ion concentration in solution. The experiments on the Co/Cu mixed synthetic solutions were performed using copper and cobalt sulphate solutions which were prepared at stoichiometric ratios of Co:Cu – 1:1, 1:5, 1:9, 5:1 and 9:1 which corresponded to metal ion concentrations of $Co^{2+}$:$Cu^{2+}$ – 0.0020:0.0020 M, 0.0020:0.0698 M, 0.0020:0.2000 M, 0.0698:0.0020 M and 0.2000:0.0020 M, respectively. The concentration levels were arbitrarily chosen in order to generate low, middle and highly concentrated solutions. These synthetic aqueous solutions were stored at room temperature (approx. 25°C). The samples were used within 48 h after preparation to minimize errors which could emanate from precipitation and container-plating of the metal ions.

The effect of competing ions in solution on $Co^{2+}$ and $Cu^{2+}$ removal efficiency using clinoptilolite, was studied using Co/Cu mixed synthetic solutions. This was done in order to ascertain the behaviour of real mine water solutions which normally contain a gangue of metals such as $Fe^{2+}$ in $CuFeS_2$ and bornite ($Cu_5FeS_4$) which may interfere with the targeted metal's removal [23]. In this study $FeCl_2$ was used as a source of $Fe^{2+}$ ions and $SiO_2$ was chosen as a source of $H_3SiO_4^-$ ions. Silica is one of the elements are abundant in the earth's crust and it forms part of the impurities that get leached out with Cu/Co ores in metal refinery techniques [23]. Its geometrical structure (tetrahedron) makes it possible to combine silica with other minerals in the earth's crust by replacing some of the O-atoms, thus making it a challenge to refine targeted minerals [24]. In order to study the effect of silica on the recovery of $Cu^{2+}$ and $Co^{2+}$ with respect to increasing silica concentration, 0.5 g and 1.0 g $SiO_2$ (0.5 g and 1.0 g) were dissolved and monitored, respectively, in the already prepared Co/Cu sulphate mixed solutions. On the other hand, the effect of presence of Si/Fe impurities on the removal of $Cu^{2+}$ and $Co^{2+}$ was pursued through the preparation of Co/Cu sulphate mixed solutions in ratios of Si:Fe of 1:1, 1:2, and 2:1 which were dissolved in water and these ratios corresponded to mass ratios (grams) of 0.5:0.5, 0.5:1 and 1:0.5.

All prepared solutions were assayed using AAS to determine the $Cu^{2+}$ and $Co^{2+}$ content before and after the adsorption experiments as described in Section 2.5.3.

### 2.8. Column adsorption experiments

The ion-exchange adsorption process experiments of $Co^{2+}$ and $Cu^{2+}$ on the clinoptilolite were performed at room temperature. Glass columns of 2 cm diameter and 30 cm of length were pre-loaded with 25 g of acid-activated clinoptilolite and a volume of 25 mL of the prepared $Co^{2+}$ and $Cu^{2+}$ bearing solutions were passed through each of the different forms of the zeolite. The contact time afforded to the experiments was 60 min. The effluent solutions were collected at 5, 10, 15, 30, 45 and 60 min intervals and were analysed for metal ion concentration using AAS.

## 3. Results and discussion

### 3.1. Effects of $SiO_2$ on $Cu^{2+}$ and $Co^{2+}$ removal efficiency using HCl-activated clinoptilolite

The addition of $SiO_2$ was found to increase the removal efficiency of $Co^{2+}$ with all the forms of clinoptilolite used in the cation removal. The results obtained with HCl-activated clinoptilolite are shown in Fig. 1.

From the results shown in Fig. 1, it can be deduced that the introduction of $SiO_2$ in the Co/Cu solutions generally enhances the removal efficiency of $Co^{2+}$ irrespective of the Co:Cu concentration in solution. This was attributed to the fact that $Cu^{2+}$ has a high affinity for the silicon compared to $Co^{2+}$, hence $Cu^{2+}$ and silicon complex forms more readily in solution. This leaves more $Co^{2+}$ ions in solution available for the exchange process. Silicon has a rather low solubility and tends to have some interaction with water molecules when dissolved in water [25]. The reactive form is silicon dioxide dissolved in water, creating the compound monosilicic acid ($H_4SiO_4$), as shown in equation (1).

$$SiO_2 + H_2O \leftrightarrow H_4SiO_4 \tag{1}$$

At neutral pH monocyclic acid can ionize as depicted in equation (2).

$$H_4SiO_4 \leftrightarrow H_3SiO_4^- + H^+ \tag{2}$$

The colloidal species is generally thought to be either silicon that has polymerized with multiple units of silicon dioxide, or silicon that has formed loose bonds with organic compounds or with other complex inorganic compounds such as $Co^{2+}$ or $Cu^{2+}$. As for which inorganic species will attach to the colloidal species depends on the cation's affinity. In this study it can be deduced that $Cu^{2+}$ had a higher affinity for $H_3SiO_4^-$ and formed complexes with it $[2Cu(H_3SiO_4)]$, which is obviously a bulky complex compared to aqueous $Co^{2+}$ ions and could not compete successfully with most of the free $Co^{2+}$ ions for the active sites on the clinoptilolite [25,26]. It is also proposed that the competitive ion may interact indirectly at the surface of the ion-exchanger by altering the ion-exchanger's surface electrical properties. For instance, it may adsorb on the clinoptilolite and make the surface more favourable for a particular metal ion present in solution. This could have occurred when more $SiO_2$ was added and $Co^{2+}$ exchange was favoured while $Cu^{2+}$ exchange was drastically reduced.

However, the 1:1 Co/Cu synthetic solution showed a slight decrease in the $Co^{2+}$ removal efficiency upon addition of $SiO_2$.

The removal trends of $Cu^{2+}$ from Si in Co/Cu solutions are depicted in Fig. 2.

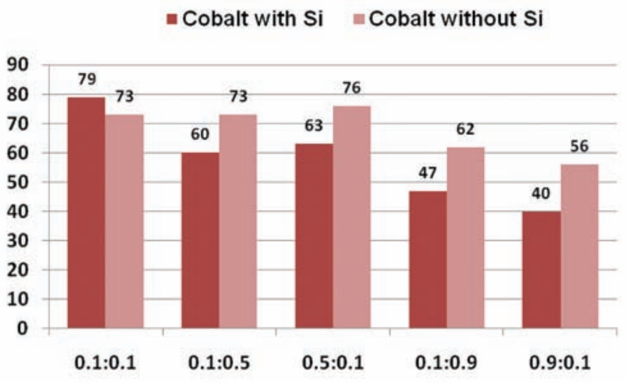

Fig. 1. Trends of $Co^{2+}$ removal from Si in Co/Cu synthetic solutions using HCl-activated clinoptilolite.

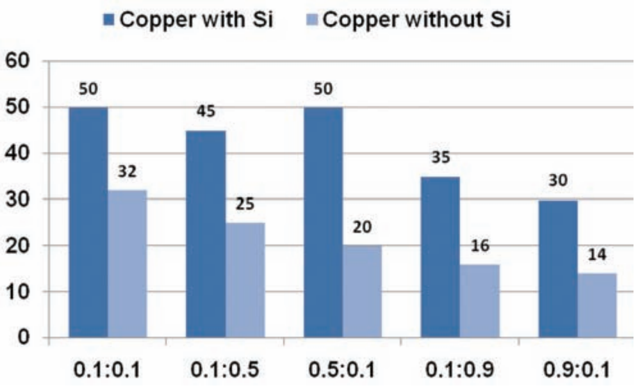

Fig. 2. Trends of $Cu^{2+}$ removal from Si in Co/Cu synthetic solutions using HCl-activated clinoptilolite.

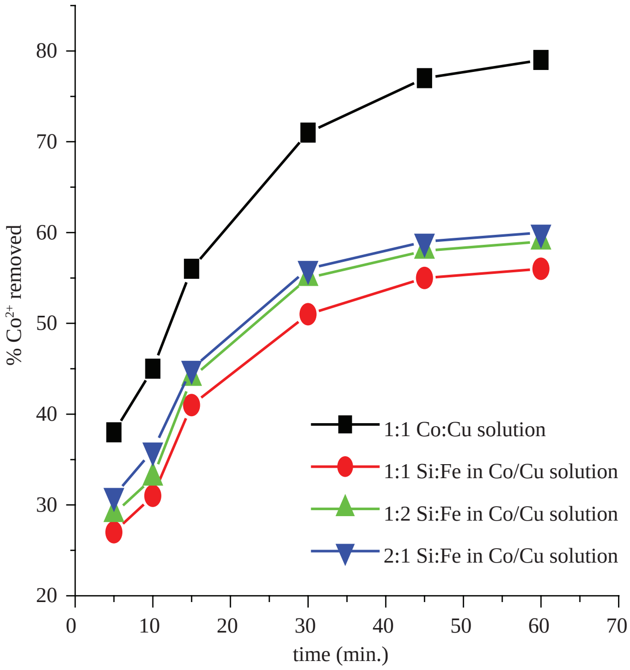

Fig. 3. $Co^{2+}$ removal from 1:1 Co:Cu, Si:Fe in Co/Cu solutions using HCl-activated clinoptilolite.

Fig. 2 shows that $Cu^{2+}$ removal efficiency was greatly reduced by the introduction of $SiO_2$. This was more evident in the solutions where the $Cu^{2+}$ concentration was less than that of $Co^{2+}$ (5:1 and 9:1 Co/Cu synthetic solutions). This can still be explained by that most of the $Cu^{2+}$ ions existed as $2Cu(H_3SiO_4)$ complex.

### 3.2. *Effects of Si/Fe on $Cu^{2+}$ and $Co^{2+}$ removal efficiency using HCl-activated clinoptilolite*

The combination of ionic species in solution may lead to different selectivity series of the targeted metals. Some data on multi-component systems clearly demonstrate that the removal efficiency of metals is greatly affected by the presence of competitive cations. The observed differences are considered to be as a result of specific attributes of the ion-exchange material and to the differences in the experimental techniques used.

In these experiments, the Co/Cu synthetic solutions without Si/Fe were treated as references for comparison purposes with solutions that contained Si/Fe impurities. **Figs. 3** and **4** show results obtained for $Co^{2+}$ and $Cu^{2+}$ removal from 1:1 Co:Cu Si:Fe in Co/Cu solutions using HCl-activated clinoptilolite.

The solutions in Figs. 3 and 4 contained equivalent concentration levels of $Cu^{2+}$ and $Co^{2+}$ ions. The pure Co/Cu solutions (without Si/Fe) impurities) had a removal efficiency of $Co^{2+}$ which was higher at 75% in relation to that of $Cu^{2+}$ at 49%. Upon adding the Si:Fe (1:1) mixture the removal efficiency of $Co^{2+}$ decreased (55%) while $Cu^{2+}$ removal efficiency was also reduced (12%). This was ascribed to $Cu^{2+}$ having a higher affinity for the added ions than $Co^{2+}$ does, hence this resulted in the $Co^{2+}$ being liberated from the Co-Cu bond and made available for adsorption. There was also an increase in removal efficiency observed with the presence of Si:Fe (1:2) in the initially pure Co/Cu solutions. However, this addition did not lower the removal efficiency beyond what was observed for the Co/Cu solutions with a Si:Fe (1:1) impurity combination. This suggests that the zeolite has less affinity for $Fe^{2+}$ compared to the $Cu^{2+}$ ions. Inglezakis and coworkers [21] studied the effects of $SO_4^{2-}$, $HPO_4^{2-}$ and $NO_3^-$ on the ion exchange of $Cu^{2+}$, $Fe^{3+}$ and $Cr^{3+}$ on natural Greek clinoptilolite. It was found that among $Cu^{2+}$, $Fe^{3+}$ and $Cr^{3+}$ the adsorption efficiency of $Cu^{2+}$ was the lowest in the presence of $HPO_4^{2-}$ and $SO_4^{2-}$ and the reason for this situation was attributed to the formation of metal-anion complexes which caused weak adsorption of these complexes.

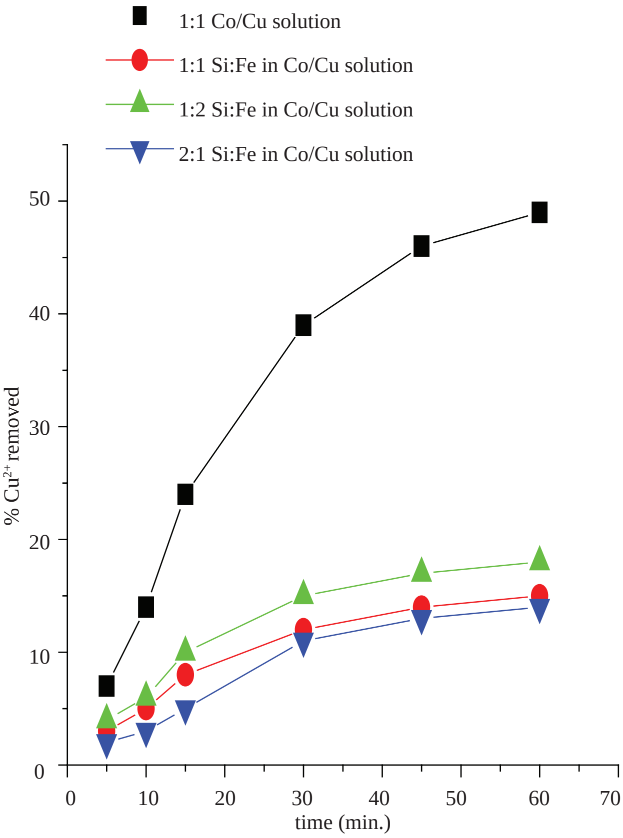

Fig. 4. $Cu^{2+}$ removal from 1:1 Co:Cu, Si:Fe in Co/Cu synthetic solutions using HCl-activated clinoptilolite.

The addition of Si:Fe (2:1) into same solution that initially contained no impurities yielded the lowest

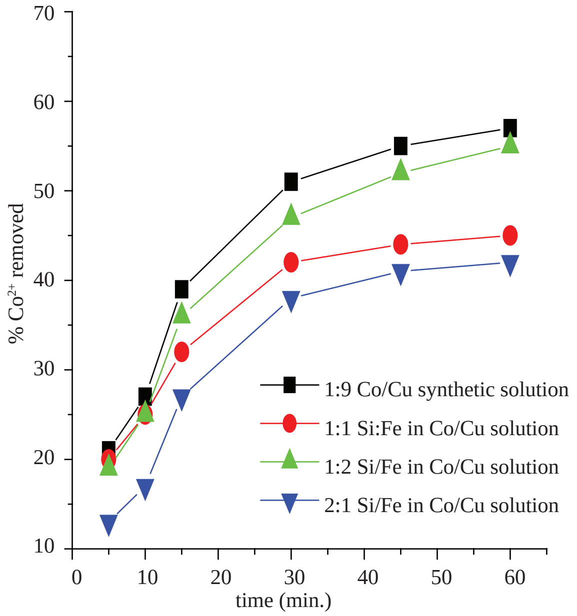

Fig. 5. $Co^{2+}$ removal from 1:5 Co:Cu, Si:Fe in Co/Cu synthetic solutions using HCl-activated clinoptilolite.

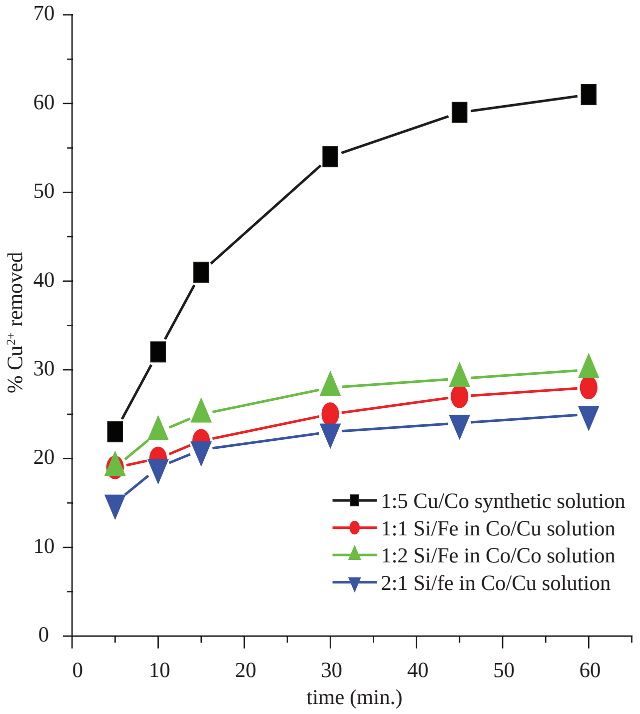

Fig. 6. $Cu^{2+}$ removal from 1:5 Co:Cu, Si:Fe in synthetic Co/Cu solutions using HCl-activated clinoptilolite.

adsorption efficiency for $Cu^{2+}$ than for $Co^{2+}$. The presence of Si in high amounts meant that more $H_3SiO_4^-$ was available to react with $Cu^{2+}$ and form $2Cu(H_3SiO_4)$ complexes which were responsible for the reduced adsorption efficiency of $Cu^{2+}$. Also, based on the Pourbaix diagram, $Fe^{2+}$ (from the dissolved $FeCl_2$) is most likely to form stable complexes at pHs up to 9 (www.corrosion-doctors.org). Since the pH of the solutions in this study was neutral, it is therefore possible that $Cu^{2+}$ formed stable aqua-complexes with $Fe^{2+}$, thus making the $Cu^{2+}$ less available for adsorption.

In solution $Fe^{2+}$ reacts in the following manner:

$$Fe_2^+ + H_2O \leftrightarrow FeOH^+ + H^+. \quad (3)$$

The $FeOH^+$ was expected to form complexes with the negatively charged species $H_3SiO_4^-$ in solution leaving the Cu and Co free for adsorption. However, the significant reduction in the $Cu^{2+}$ adsorption efficiency can be attributed to the stability of the complexes formed. It is suspected that the complex formed between $H_3SiO_4^-$ and $Cu^{2+}$ forms faster and is more stable than the complex formed between $FeOH^+$ and $H_3SiO_4^-$.

The solutions in Figs. 5 and 6 contained more $Cu^{2+}$ than $Co^{2+}$ ions (1:5). Almost the same trend with the Si/Fe-doped solutions is observed in these solutions, i.e., they showed an ease of removal for $Co^{2+}$ than for $Cu^{2+}$.

An introduction of more $SiO_2$ into the Co/Cu mixed solutions reduced the removal efficiency of $Cu^{2+}$ and favoured that of $Co^{2+}$ since the percentage removal was much higher than that observed for the same metal ion in the pure Co/Cu solutions. This may be as a result of the $SiO_2$ attaching itself to the $Cu^{2+}$ with the $Co^{2+}$ being released from the Co-Cu bond and the $Co^{2+}$ – which has a lower affinity for the $Fe^{2+}$ compared to $Cu^{2+}$ – becoming available for adsorption. An introduction of Si:Fe in the ratio of 1:1 lowered the $Co^{2+}$ and $Cu^{2+}$ removal efficiencies. The $Cu^{2+}$ removal efficiency drop was attributed to the nature of the complexes it forms with the impurities i.e. probably the complexes are too bulky to move in solution towards the adsorbent or the sizes of complexes are too bulky to pass through the adsorbent's pores and therefore remain in the solution unadsorbed [27].

Since there were more $Cu^{2+}$ ions in these solutions than $Cu^{2+}$ ions and $Cu^{2+}$ ions had a higher affinity for the impurities than $Co^{2+}$. it would be expected that the $Co^{2+}$ should have much higher removal efficiencies than those obtained in these experiments. The reason for the deviation from the expected observations may have been due to the fact that even after the proposed complex-formation which the $Cu^{2+}$ ions partake in, a good proportion of the $Cu^{2+}$ ions still remains in solution and re-bonds with the $Co^{2+}$ ions that would otherwise have been available for adsorption.

In Figs. 7 and 8, the solutions contained more $Co^{2+}$ ions than $Cu^{2+}$ ions (5:1).

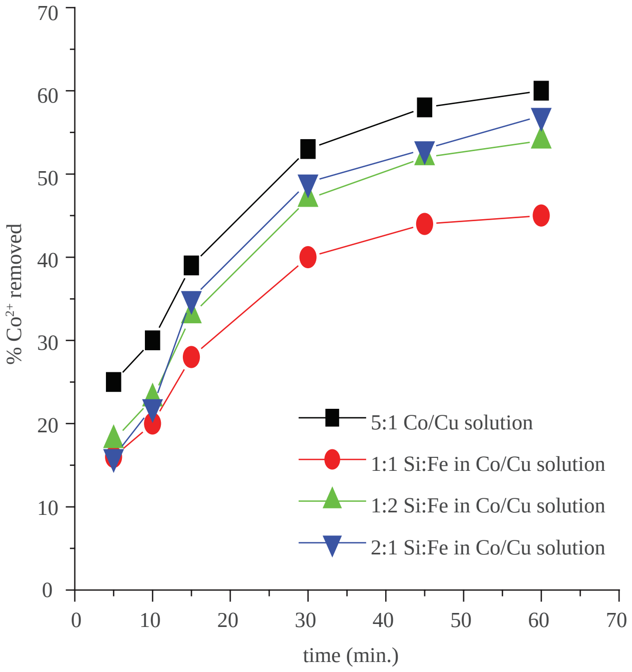

Fig. 7. $Co^{2+}$ removal from 5:1 Co:Cu, Si:Fe in Co/Cu solutions using HCl-activated clinoptilolite.

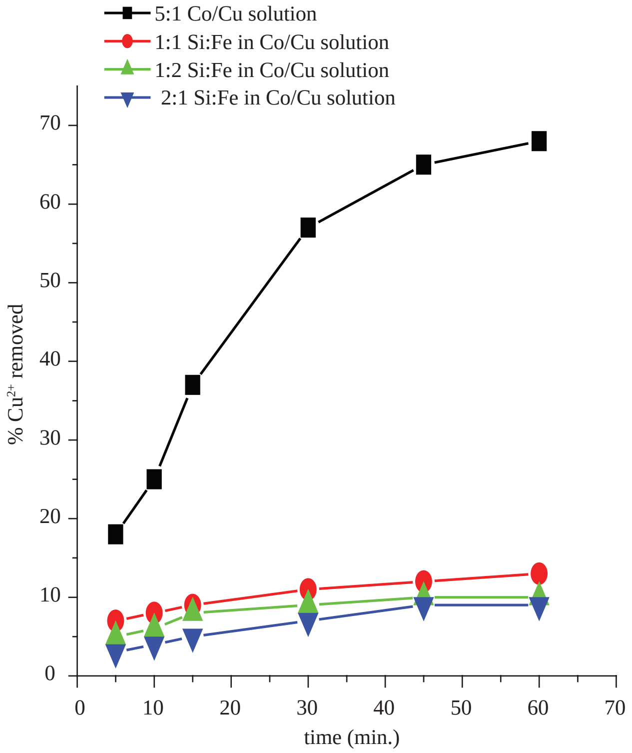

Fig. 8. $Cu^{2+}$ removal from 5:1 Co:Cu, Si:Fe in Co/Cu synthetic solutions using HCl-activated clinoptilolite.

The percentage removal efficiencies obtained with the 5:1 Co/Cu mixed solution with no impurities were 73% for $Cu^{2+}$ and 63% for $Co^{2+}$, making the recovery of $Cu^{2+}$ to be more favoured over that of $Co^{2+}$. However, the introduction of Si:Fe in the ratio of 1:1 lowered the recovery of $Cu^{2+}$ from 73% to 10% while a ratio of 1:2 Si:Fe impurities lowered the recovery of $Cu^{2+}$ to 7% and that of 2:1 Si:Fe ratio brought it down to 4%. In the light of the fact that there were more $Co^{2+}$ than $Cu^{2+}$ ions in these solutions, such low removal efficiencies could have been caused by the added impurities forming complexes with the abundant $Cu^{2+}$ ions since the impurities have a high affinity for the copper ions as already stated earlier. This complex-formation almost exhausts the already few free amounts of $Cu^{2+}$ present in the solutions thus resulting in the exchange of very low concentrations of $Cu^{2+}$ ions. If such is the case, it would also be expected that the recorded efficiencies for $Co^{2+}$ removal should be raised to very high removal efficiencies than what was actually obtained which however, does not happen. This may be due to the fact that as much as $Co^{2+}$ is noted to have less affinity for the impurities than $Cu^{2+}$, it is also expected to form complexes with impurities only at a lower rate than $Cu^{2+}$, thus its adsorption is slightly affected.

The solutions for Figs. 9 and 10 contained high concentrations of $Co^{2+}$ ions than $Cu^{2+}$ ions in the ratio of Co:Cu (9:1).

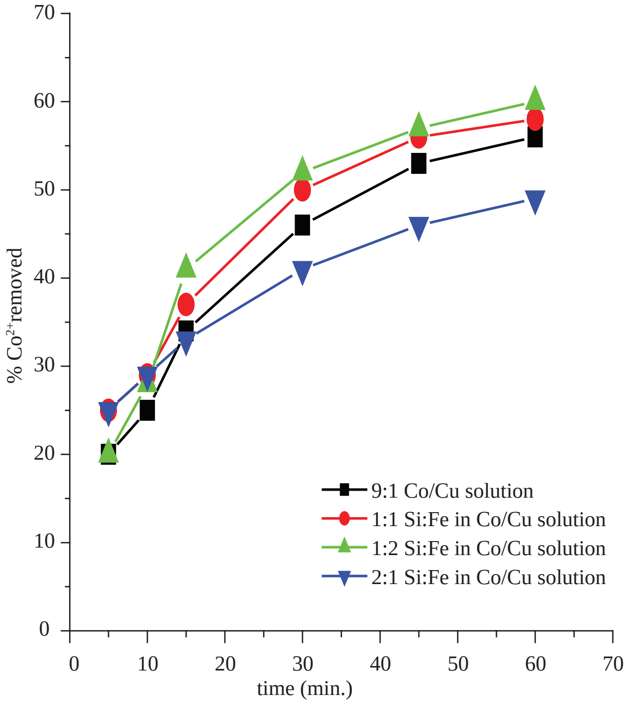

Fig. 9. $Co^{2+}$ removal from 9:1 Co:Cu, Si:Fe in Co/Cu synthetic solutions using clinoptilolite.

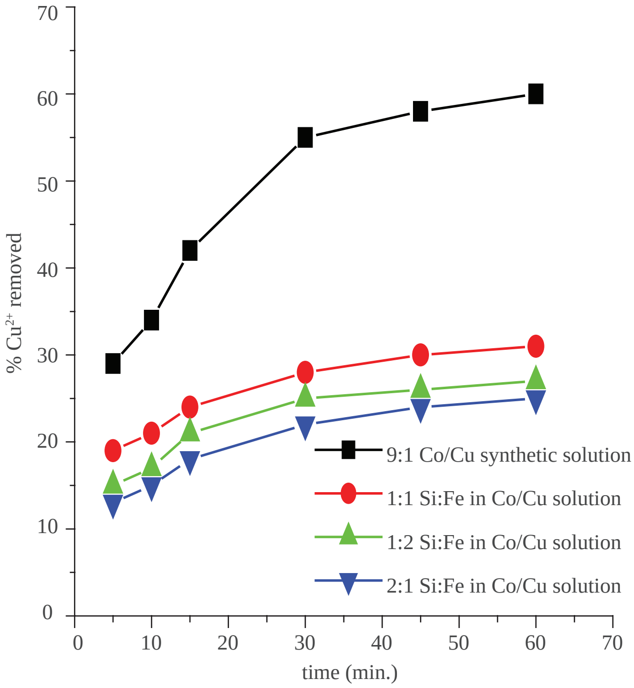

Fig. 10. $Cu^{2+}$ removal from 9:1 Co:Cu, Si:Fe in Co/Cu synthetic solutions using KCl-activated clinoptilolite.

The observed removal efficiency of $Co^{2+}$ from the 9:1 Co/Cu solution was 56% while that of $Cu^{2+}$ is 57%. An introduction of impurities in these solutions drastically reduced the removal efficiency of $Cu^{2+}$ to 29% with the 1:1 Si:Fe in Co/Cu solutions, 25% with the 1:2 Si:Fe in Co/Cu solutions and 23% with 2:1 Si:Fe in Co/Cu solutions. On the other hand, the removal efficiency of $Co^{2+}$ was enhanced in the 1:1 and 1:2 Si:Fe in Co/Cu solutions. The reduction in the removal efficiencies for $Cu^{2+}$ removal was due to the added $FeCl_2$ and $SiO_2$ forming complexes with the $Cu^{2+}$ ions as already mentioned earlier. The enhancement in the removal efficiency of $Co^{2+}$ with the addition of impurities could again be due to the liberation of $Co^{2+}$ ions from the Co-Cu bonds. This was more pronounced where Si:Fe (1:2 ratio) of impurities were added into the solution. This phenomenon appears to be a stoichiometric reaction which largely depends on the amounts of impurities available to form complexes with the targeted metals which results in only a few of the metal ions being adsorbed by the adsorbent.

As pointed out earlier, the combination of ionic species in solution may lead to different selectivity patterns; this was observed with the Si/Fe in Co/Cu synthetic aqueous solutions studied. However, this does not explain the ease of removal of $Co^{2+}$ from the Si/Fe in Co/Cu synthetic solutions and the less efficiency of $Cu^{2+}$ removal. The $Co^{2+}$ was removed with less difficulty from solutions where the Cu:Co ratio quantities were equal or if there was a higher concentration of $Co^{2+}$ ions than $Cu^{2+}$ ions. In a typical multi-component system, Si/Fe and Co/Cu aqueous solutions, the complexes formed by these cations may not be as simple as the ones in the Co/Cu non-mixed aqueous solutions. Complexes with metal impurities may be attached to other complexes leading to the formation of even bulkier complexes. Such complex-formation largely depends on the ability of the competing ions in solution to attract other ionic species to themselves and the length of time taken to keep these species in the complex state.

This factor is important since the ion-exchange process is time dependent i.e. the longer the complex stays in its bulkiest forms the more delayed or even less likely its loading into the ion-exchanger, regardless of its normally small hydrated radius, which is supposed to favour it uptake. While the presence of impurities was observed to lower the metal uptake efficiency, the degree of interference in the ion-exchange process was largely dependent on the type of impurity present in the solution i.e. where there was more $SiO_2$ than $FeCl_2$, $Co^{2+}$ removal was enhanced and vice versa. The coordination numbers of the impurities may provide a plausible explanation [28]. These numbers determine: (i) the complexomatrix of the cation whether or not it will form a stable complex with that particular impurity (ii) the type of hydrated ions that the impurity forms with water molecules and (iii) the enthalpy of hydration of the impurity. The $Cu^{2+}$ ion is therefore expected to form more stable complexes since its coordination number can be increased to 6 due to the availability of s, p and d-orbitals. Complexes formed in this manner are even more stable compared to complexes formed by an ordinarily 6-coordinated cation such as $Co^{2+}$ [27]. In most cases, hexa-coordinated cations form labile complexes compared to tetra-coordinated one as illustrated in (4)

$$[M(H_2O)_x \ldots l(H_2O)]^{n+} \tag{4}$$

where $M$ is either $Cu^{2+}$ or $Co^{2+}$ present in solution and $l$, is the impurity that has been added into the Co/Cu synthetic solution.

The strength of the bond in the complex depends on the coordination number of the metal in the solution [27]. It is probable that the reason why the $Co^{2+}$ cation was more favoured in the presence of impurities was due to $Cu^{2+}$ ions forming bulky and stable compounds with the impurities in solution, thus isolating the $Co^{2+}$ cations to form more labile hexa-aqua complexes that favour $Co^{2+}$ sorption. Some of the $Cu^{2+}$ ions were also exchanged but this process was evidently slower.

An interaction between metal ions and the complexing ligands is one factor which is based on the origin and the strength of the interaction. In this regard, metal-ligand complexes may form in solution (ion-pairing) and weakly adsorb on the exchanger's surface or not form at all. Thus, the formation of soluble complexes may be considered to compete with reactions forming the so-called ''surface complexes'', leading to a decrease in the ion-exchange of the targeted ion compared to a system that contains no competitive ions. The decreased removal efficiency of $Cu^{2+}$ in the presence of impurities can be attributed to the assertion that it is possible that the $Cu^{2+}$ complexes were formed on the surface of the clinoptilolite and subsequently hindered the exchange of $Cu^{2+}$ ions.

Another argument is based on the types of complexes formed by $d^9$ configured elements. The $d^9$ configuration makes $Cu^{2+}$ to be subject to Jahn-Teller distortion if placed in a regular octahedral or tetrahedral environment which results in a profound effect on its stereochemistry [27]. $Cu^{2+}$ appears to form complexes such as $[Cu(H_2O)_6SiCl_6]$ that are truly undistorted octahedral forms. In this type of complex, 75% of the octahedral $[Cu(H_2O)_6]^{2+}$ complexes are distorted while 25% are regular. The complex $[Cu(H_2O)_6SiCl_6]$ is assumed to be formed in the Si/Fe in Co/Cu synthetic aqueous solutions and in the real solutions. In this study, the non-distortion of this complex was observed not to favour the ion-exchange of $Cu^{2+}$ by the different forms of clinoptilolite. The poor exchange of $Cu^{2+}$ can be attributed to this factor. It could be that if distortion of the Cu-complex shape occurred it would have conformed to the zeolite channels' shape and favoured its exchange. Another factor that contributes to $Cu^{2+}$ being exchanged the least is that $Cu^{2+}$ forms chlorocomplex ions such as $[CuCl_4]^{2-}$ with $Cl^-$ ions from the added $FeCl_2$ impurity [29]. This theory predicts the tetragonal elongated octahedron and square geometries for the attachment of this anion to smaller cations such as $Fe^{2+}$. In such cases the $[CuCl_4]^{2-}$ anion cannot be readily isolated due to the high attractive forces exhibited by small cations such as the $Fe^{2+}$ attached to it [29]. This factor does not favour the exchange of $Cu^{2+}$ ions by the clinoptilolite.

Another possible explanation for the non-preference of $Cu^{2+}$ could be that $Fe^{2+}$, in the absence of complexing ions forms $[Fe(H_2O)_6]^{2+}$, has an octahedral geometry which in the presence of $Cl^-$ ions from the $FeCl_2$ forms trans $[FeCl_2(H_2O)_4]$ ions in solution. The introduction of $FeCl_2$ in the Co/Cu synthetic solutions was observed to markedly reduce the removal efficiency of $Cu^{2+}$. The aqueous solution also contained $SO_4{}^{2-}$ ions from the copper (II) and cobalt (II) sulphate salts which are known to hinder ion-exchange. It is possible that a bulky complex forms in aqueous solution in the presence of $SO_4{}^{2-}$ and $Cl^-$ anions. The complex that is supposedly formed has the Mohr's salt $NH_4)_2[Fe(H_2O)_6(SO_4)_2$ structure which can be written as $Cu[Fe(H_2O)_6](SO_4)_2$ [29]. This is obviously a very bulky complex and is expected to migrate with great difficulty in solution; hence the removal of $Cu^{2+}$ is expected to be greatly reduced. The fact that there was some $Cu^{2+}$ removed from these solutions can be attributed to the half-life of the complex which suggests that the half-life of the complex was within the time afforded for the ion-exchange experiments in this study. The $Co^{2+}$ is also capable of forming a similar complex since it is also divalent. However, its removal efficiency was not negatively affected by the complex formation. The $Cu^{2+}$ compared to $Co^{2+}$ probably had more affinity for the $[Fe(H_2O)_6]^{2-}$ anions when considering the coordination numbers of the two cations (4 for $Cu^{2+}$ and 6 for $Co^{2+}$). As the $Cu^{2+}$ complexation occurred, most of the $Co^{2+}$ ions were liberated from a possible Co-Cu interaction and made available for the ion exchange process. This resulted in a more pronounced reduction in $Cu^{2+}$ removal efficiency in solutions where there were more $Co^{2+}$ ions than $Cu^{2+}$ ions.

## 4. Conclusions

The removal efficiencies of $Cu^{2+}$ and $Co^{2+}$ were affected by the presence of the two cations existing in a single solution at different concentrations. It was concluded that the $Cu^{2+}$ and $Co^{2+}$ cations were formed as high-spin aqua complexes in aqueous solution and the hydrated ion radius of the aqua-complex size formed in solution was dependent on the coexisting competitive ions. Impurities in the form of $SiO_2$ and $FeCl_2$ negatively affected the removal efficiency of $Cu^{2+}$ while they enhanced the removal efficiency of $Co^{2+}$. On the other hand, $SiO_2$ as an impurity alone did not favour the removal efficiency of $Co^{2+}$ ions. The results obtained for the removal of $Cu^{2+}$ and $Co^{2+}$ in the presence of $H_3SiO_4^-$ and $Fe^{2+}$ as competitive ions in the aqueous solutions greatly affected the removal efficiency of $Cu^{2+}$ ions, especially when the concentration of $Cu^{2+}$ was very low. However, $H_3SiO_4^-$ and $Fe^{2+}$ appeared to enhance the removal efficiency of $Co^{2+}$ to some extent.

## Acknowledgements

Funding from the National Research Fund (NRF), University of Johannesburg and ESKOM's Tertiary Education Support Programme (TESP) is gratefully appreciated.

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