Contribution of cobalt ion precipitation to adsorption in ion exchange dominant systems

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Abstract

Contribution of metal ion precipitation to the adsorption of Co^{2+} ions from aqueous solutions onto sepiolite has been analyzed as a function of pH. Abstraction and precipitation isotherms are constructed to isolate the precipitation of cobalt from the real adsorption. The contribution of all cobalt species against pH is calculated from the available solubility products or acid constants. It is found that at pH 8.2, which is the onset of cobalt hydroxide precipitation, the distribution of adsorbed cobalt species is as follows: 92% Co^{2+}, 7% $CoOH^+$ and 1% $Co(OH)_2$. The experimental values are in accord with the calculated uptake of cobalt species onto sepiolite. Adsorption of cobalt ions onto sepiolite before precipitation of cobalt is governed by ion exchange between the released Mg^{2+} ions from sepiolite matrix and those adsorbed Co^{2+} ions; this behavior differs from typical oxide (titanium dioxide) and silicate (quartz) minerals. However, adsorption of cobalt onto the same materials including sepiolite follows the same trend after the region of cobalt precipitation despite distinct differences in their charge profiles.
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1. Introduction

The removal of heavy metal ions from industrial wastewaters using different adsorbents is currently of great interest [1–3]. Activated carbon has been tested for the removal of inorganic ions from aqueous solutions (4, 5, 1). Generally the adsorption density of inorganic species onto activated carbon varies significantly with pH. The magnitude of adsorption increases abruptly at a specific pH, which is the characteristic of acid-base behavior of activated carbon. Netzer and Hughes [4] investigated the adsorption of Co^{2+} ions from wastewaters onto activated carbon and found a decrease in Co^{2+} adsorption in the presence of Pb^{2+} and/or Cu^{2+} ions.

However, in order to minimize processing costs for these effluents, recent investigations have focused on the use of low cost adsorbents [5–10]. Adsorption isotherms of Co^{2+} in aqueous silica and rutile suspensions were reported by James and Healy [11]. Adsorption of Co^{2+} ions was shown to increase with increasing the concentration of Co^{2+} ions and pH. They developed an ion–solvent interaction model, which accounts for the adsorption energies including electrostatic, specific chemical interaction and solvation terms.

Adsorption of various metal ions, i.e., Cd, Cu and Zn onto sepiolite has been studied for the purpose of remediation of polluted soils [10]. Adsorption efficiency of heavy metal removal from sepiolite has been found to follow the order of Pb < Cd < Co < Zn < Cu [12] and Ni < Cd < Zn [13]. Adsorption of cobalt onto oxide and silicate minerals, which have distinct differences in their chemical composition and zeta potential profiles [14], has been reported to follow a similar trend both before and after the onset of cobalt precipitation [11]. However, the

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Table 1
Chemical analysis of Sivrihisar sepiolite

Component	SiO$_2$	MgO	CaO	Al$_2$O$_3$	Fe$_2$O$_3$	Na$_2$O	K$_2$O	TiO$_2$	LOI
wt.%	51.93	24.20	0.12	1.52	0.70	0.12	0.33	0.08	21.00

major difference between these minerals and sepiolite is the ability of magnesium in the octahedral sheet of sepiolite undergoing ion exchange with cobalt ions. However, most studies usually do not account for the magnitude of precipitation when constructing an adsorption isotherm or calculate the amount adsorbed in a typical fixed bed column reactor.

The aim of the present investigation is, therefore, to study the adsorption mechanism of various Co^{2+} species onto natural sepiolite against pH in the light of calculated and available thermodynamic data taking account the magnitude of cobalt precipitation and compare it with the relevant literature.

2. Experimental

2.1. Materials

The brown sepiolite used, in this study, is a product of Mayas Mining Company operating in Eskişehir - Sivrihisar region of Turkey. The Chemical analysis shown in Table 1 together with the XRD data indicates the presence of minute amounts of dolomite and calcite impurities. The specific surface area, medium particle size, percent porosity and average pore diameter of this sepiolite are determined, respectively, as 68 m^2/g, 2 μm, 70% and 37 Å.

2.2. Methods

Adsorption tests as a function of pH were conducted in 100 ml beakers. A sepiolite sample of 5 g was mixed in 100 ml solution of desired levels of Co(NO$_3$)$_2$ and shaken for 15 min on a magnetic stirrer. The pH value of solutions was continuously monitored during the conditioning period of 15 min with 0.1 M HNO$_3$ or 0.1 M/l NaOH. The syringes were then fitted to filter holders of 0.5 μm in pore size and filtered. Collected filtrates were used in the analysis of supernatant for Co^{2+} and Mg^{2+} ions using Inductively Coupled Plasma (ICP) spectrophotometer. The amount of Cobalt or its various species adsorbed onto sepiolite was calculated from the difference between the initial and the residual concentration in solution as follows [15]:

$$\Gamma = \frac{(C_i - C_r)V}{mS\,1000} \qquad (1)$$

where C_i and C_r represent the initial and residual concentrations in M/l, m the amount of solid in grams, V the volume of the solution in ml, S the specific surface area of sepiolite in m^2/g and Γ the adsorption density in M/m^2.

Distilled and deionized water with a conductivity value of 1.5×10^{-6} mhos/cm was used in all experiments. Experiments were conducted at $20 \pm 1\,°C$.

3. Results and discussion

3.1. Precipitation of cobalt species

Cobalt ions begin precipitation in the vicinity of pH 8 depending upon the initial total cobalt concentration. In order to determine the onset of pH at which precipitation is initiated, the literature value on the solubility product of cobalt hydroxide is calculated using the initial concentration of 2.5×10^{-3} M/l as follows [16]:

$$Co(OH)_2 \rightarrow Co^{2+} + 2OH^-, \quad K_s = 6.3 \times 10^{-15} \quad [16] \quad (2)$$
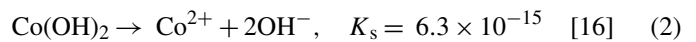
$$[Co^{2+}][OH]^{-2} = 6.3 \times 10^{-15} \qquad (3)$$

This calculated value indicates that at 2.5×10^{-3} M/l initial cobalt concentration cobalt hydroxide starts precipitating at pH 8.2.

3.2. pH-dependent adsorption experiments

The effect of pH on adsorption of cobalt ions onto sepiolite at 2.5×10^{-3} M/l of initial cobalt ion concentration is presented in Fig. 1. As evident from Fig. 1, abstraction increases up to pH 6.5, exhibits a significant increase in the pH range of 6.5–8, increases marginally and then forms a plateau above pH 8.5. At initial cobalt concentration of 2.5×10^{-3} M/l and pH 8.2, cobalt ions undergo a number of hydrolysis reactions leading to various species depending upon the initial cobalt concentration and pH: CoOH$^+$, Co(OH)$_{2aq}$, Co(OH)$^{3-}$ [17]. Gutierrez and Fuentes [18] reported the adsorption of cobalt ions onto Ca-montmorillonite to increase significantly above pH 8; this has been ascribed to the deposition of cobalt hydroxy precipitates. Similar comments were made by Bangash et al. [19].
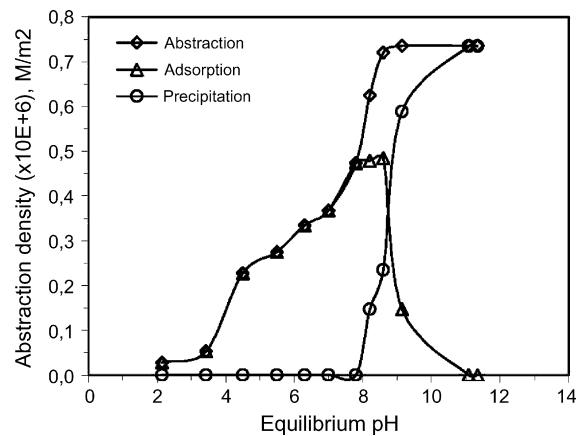

Fig. 1. Abstraction (adsorption + precipitation) of cobalt with sepiolite vs. equilibrium pH. $C_i = 2.5 \times 10^{-3}$. Conditioning time: 15 min, solid-liquid ratio = 0.05, $T = 20\,°C$.
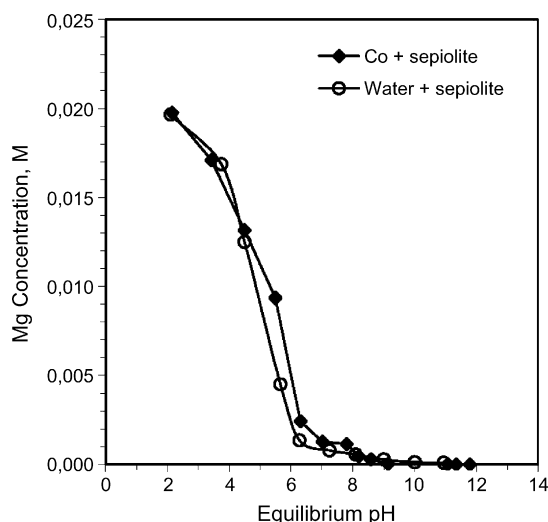
Fig. 2. Dependence of pH on Mg^{2+} ion release in water–sepiolite and cobalt–sepiolite systems.

In both studies, the contribution of precipitation to adsorption at high pH has not been accounted for and thus cannot represent the real adsorption but rather than abstraction. For this reason, the uptake of cobalt above pH 8.2 in Fig. 1 is separately analyzed as abstraction and adsorption. Here, abstraction is defined as the total depletion of cobalt from the solution in the form of both adsorption and precipitation as follows [20]:

$$Abstraction = Adsorption + Precipitation$$

Accordingly, in order to obtain a net adsorption isotherm, precipitation values need to be subtracted from those of abstraction. The precipitation of cobalt hydroxide was considered on quartz for calculating the real adsorption densities (11).

Abstraction tests conducted at natural pH indicated that a significant ion exchange between the added cobalt ions and those released from the octahedral sheet occurs [21]. Since sepiolite suspensions undergo acid–base reactions in the vicinity of natural pH, the desired pH was kept constant during conditioning by introducing appropriate amounts of acid (HCl) or base (NaOH) for 15 min followed by centrifugation for 5 min. The Mg^{2+} ion concentration and pH of the supernatant were simultaneously measured. Fig. 2 illustrates the release pattern of magnesium ions both in the absence and presence of cobalt ions. The release of cobalt into solution decreases with increasing pH and then becomes constant near the natural pH of 8. The H^+ ions of the acid used in adjusting the pH of solution undergo an ion exchange with those of Mg^{2+} ions in the octahedral sheet and lead to the release substantial amounts of Mg^{2+} ions. The concentration of Mg^{2+} ion at pH 2 and 12 are 1.96×10^{-2} and 8×10^{-5} M/l, which, respectively, corresponds to the calculated pH values of 9.22–10.85 for $Mg(OH)_2$ precipitation. Accordingly, when Fig. 2 is examined only in the last three pH values was the precipitation observed. At higher pH values Mg^{2+} ions released due to ion exchange process reacted with OH^- ions to produce the $Mg(OH)_2$ precipitate. However, as seen in Fig. 2, since the concentration of Mg^{2+} is so low

at high pH, the formation of $Mg(OH)_2$ precipitate is unlikely. The quantity of dissolved Mg^{2+} ions in water–sepiolite system is higher than that in Co^{2+}–water–sepiolite system up to pH 5 due to the release of additional Mg^{2+} ions by the H^+ ions of the acid used for adjusting pH. However, this effect ceases in the pH range of 5–8.2 above which the amount of dissolved Mg^{2+} ions becomes equal to the adsorbed Co^{2+} ions onto sepiolite. Consequently, in this pH interval, the adsorption mechanism is ascertained as the ion exchange; the exchange mechanism is, however, not indicative at pH values higher than pH 8.2 due to the hydrolysis of Co^{2+} ions as insoluble complexes. A measurement technique such as ion selective electrode, which is capable of distinguishing the free ion concentration, can be useful in this regard.

3.3. pH–concentration diagrams

The slope of the plateau in the adsorption isotherms given elsewhere at 2.5×10^{-3} M initial cobalt concentration approaches unity [21]. By taking this as a constant, pH-concentration diagrams have been constructed. The reactions used and the corresponding equilibrium constants are given in Table 2.

The following hydrolysis reactions can be written in view of Table 2. It should be noted that no activity correction was applied.

$$K_1 = \frac{[Co(OH)^+][H^+]}{[Co^{2+}]} \tag{3}$$

$$K_2 = \frac{[Co(OH)_{2aq}][H^+]}{[Co(OH)^+]} \tag{4}$$

$$K_3 = \frac{[Co(OH)_3{}^-][H^+]}{[Co(OH)_{2aq}]} \tag{5}$$

The total ion concentration in the solution is equal to the total number of species given in Eqs. (3)–(5). Here $C_i = 2.5 \times 10^{-3}$ M/l

$$[Co^{2+}] + [Co(OH)^+] + [Co(OH)_{2aq}] + [Co(OH)_3{}^-] = C_i \tag{6}$$

Using Eqs. (3)–(6), each species in solution has been calculated.

$$[Co^{2+}] = \frac{C_i[H^+]^3}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3} \tag{7}$$

Table 2
Cobalt hydrolysis reactions and equilibrium constants

Hydrolysis reactions	K	$\log K$
$Co^{2+} + H_2O \Leftrightarrow Co(OH)^+ + H^+$	K_1	−9.6
$Co(OH)^+ + H_2O \Leftrightarrow Co(OH)_{2aq} + H^+$	K_2	−9.2
$Co(OH)_{2\,aq} + H_2O \Leftrightarrow Co(OH)_3{}^- + H^+$	K_3	−12.7

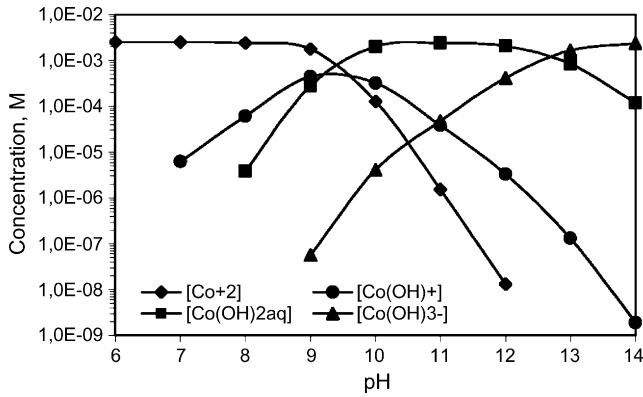Fig. 3. pH–concentration diagram for cobalt species at $C_i = 2.5 \times 10^{-3}$ mol/l.

$$[Co(OH)^+] = \frac{C_i K_1 [H^+]^2}{[H^+]^3 + K_1 [H^+]^2 + K_1 K_2 [H^+] + K_1 K_2 K_3} \quad (8)$$

$$[Co(OH)_{2aq}] = \frac{C_i K_1 K_2 [H^+]}{[H^+]^3 + K_1 [H^+]^2 + K_1 K_2 [H^+] + K_1 K_2 K_3} \quad (9)$$

$$[Co(OH)_3^-] = \frac{C_i K_1 K_2 K_3}{[H^+]^3 + K_1 [H^+]^2 + K_1 K_2 [H^+] + K_1 K_2 K_3} \quad (10)$$

Data from Eqs. (7)–(10) have been plotted in the form of pH–C in Figs. 3 and 4.

As apparent from Fig. 3, the Co^{2+} species remains dominant until pH of about 8 and then decreases sharply, $Co(OH)^+$ species exhibits a maximum around pH 9 with a slight decrease above it. Among the hydrolysis products $Co(OH)_{2aq}$ appears to be the most significant; this species undergoes precipitation in the form of $Co(OH)_{2(s)}$ as governed by its solubility product given in Eq. (3).
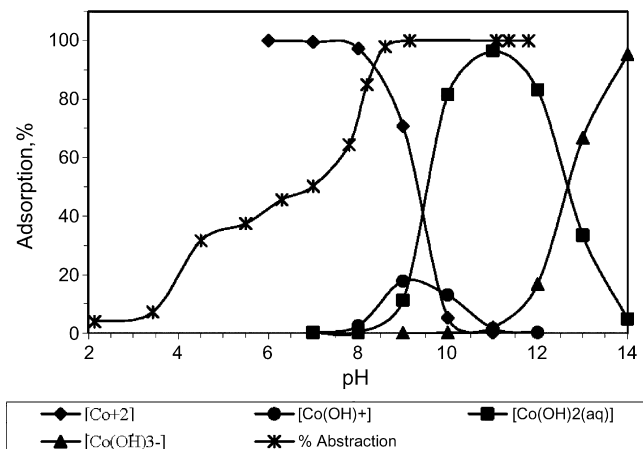

Fig. 4. Percent distribution of each cobalt complex against pH and the corresponding abstraction curve of cobalt.

Fig. 4 combines the percent distribution of cobalt complexes against pH and the abstraction curve in Fig. 1. The abstraction curve reveals that the free Co^{2+} ions have been completely adsorbed by sepiolite until the pH value of 8.2 above which adsorption gradually decreases and finally attains a plateau. In other words, above pH 8.2, the Co^{2+} ions in solution decreases and the other hydroxyl species in various forms and concentrations, $Co(OH)^+$, $Co(OH)_{2aq}$ and $Co(OH)_2^-$ appear; the $Co(OH)_{2aq}$ takes over and eventually precipitates as $Co(OH)_{2(s)}$.

As evident from Fig. 1, adsorption and abstraction curves overlap at pH 8.2 above which a decrease in adsorption due to precipitation of cobalt hydroxide particularly above pH 9.5 occurs. The results reveal that the distribution of adsorbed cobalt species at natural pH 8.2 is as follows: 92% Co^{2+}, 7% $CoOH^+$ and 1% $Co(OH)_2$; this distribution is 36.5, 16.5 and 47.0% at pH 9.5. The value of $Co(OH)_2$ reaches 100% at pH 11. These results are in line with those reported by James and Healy [11].

The adsorption of ions, such as Co^{2+}, La^{3+} and Th^{4+} onto colloidal silica and titanium dioxide was reported by James and Healy [11]. They developed a qualitative relationship between the pH of adsorption and that of hydrolysis and established the occurrence of three distinct regions in the electrokinetics data with increasing pH; these were referred as charge reversals (CRs). The first one (CR1) represents the point of zero charge (pzc) of the solid itself, the second was attributed to the specific adsorption of the partially hydrolyzed metal ions (CR2) and at higher pH the formation of metal hydroxide precipitates which partially or completely cover the solid surface. Similar results for Co, Cd and Cu ions were reported by Hunter and James [14] for kaolinite system. While the CRs vary with the initial ion concentration, CR1 for kaolinite is around 2 and CR2 and CR3 are in the range of 7–9 depending upon the initial Co ion concentration in the system.

Contrary to the results on silica reported by James and Healy, where adsorption is lower prior to the onset of precipitation, in the case of sepiolite, which is dominated by ion exchange up to pH 7, most of the adsorption takes place before the onset of metal hydroxide precipitation. However, in the case of silica system, precipitation and adsorption continue at a similar rate in the region of precipitation. The formation of surface precipitation followed by bulk precipitation has important implications in flotation and wastewater treatment systems [22]. Also the formation of secondary precipitates plays an important role in the retention of cobalt by clay minerals [23,24].

In fact, electrokinetic data reported by Kara et al. [21] for sepiolite/cobalt system show no indication of the three regions prevalent in silica and titanium dioxide systems. This is solely attributed to the ion exchange properties of sepiolite which maintains electrical neutrality upon exchanging cobalt with magnesium up to pH 8.2 above which ion exchange is drastically reduced. Fig. 5 illustrates adsorption of cobalt ions onto sepiolite, titanium dioxide and quartz against pH; data for quartz and titanium dioxide are taken from James and Healy [11]. It is clear that adsorption of cobalt onto all the three minerals overlap about above 7.5 irrespective the type of minerals but exhibits differences below this pH. Cobalt curves for similar initial concentration curves of quartz and titanium dioxide are
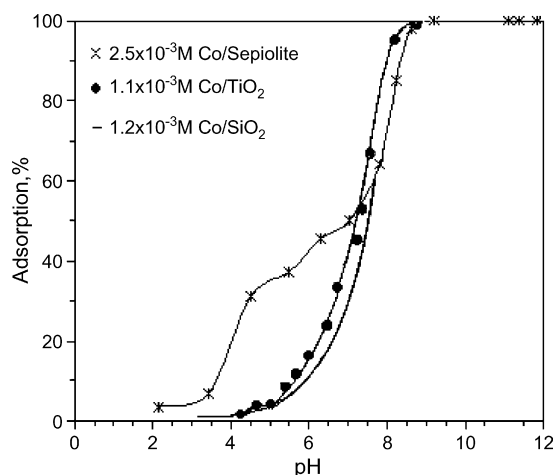
Fig. 5. Adsorption of cobalt ions onto sepiolite, titanium dioxide and quartz against pH; data for quartz and titanium dioxide are taken from James and Healy [11].

very close though at higher cobalt levels the curves for quartz show marginally higher adsorption/abstraction trend. Interestingly, the adsorption curve for sepiolite yields a distinctly higher adsorption curve in the pH range of 4–6 due to Co undergoing ion exchange with Mg ion in the octahedral sheet of sepiolite. Otherwise, it is envisaged that adsorption of cobalt onto sepiolite, quartz and titanium dioxide would have coincided throughout the pH range despite significant differences in their isoelectric points.

4. Conclusions

Contribution of metal ion precipitation to the adsorption of Co^{2+} ions from aqueous solutions onto sepiolite has been evaluated as a function of pH using the available solubility products. Abstraction and precipitation isotherms were constructed to isolate the precipitation of cobalt from the real adsorption.

The distribution of cobalt species as a function pH and their contribution to adsorption is calculated. Apart from ion exchangeable minerals such as sepiolite, oxide and silicate minerals whose potential determining ions are H^+ and OH^-, exhibit a similar uptake of cobalt both before and after the pH of precipitation. It is shown that at pH 8.2, which is the onset of cobalt hydroxide precipitation, the distribution of adsorbed cobalt species is as follows: 92% Co^{2+}, 7% $CoOH^+$ and 1% $Co(OH)_2$. The calculated and experimental adsorption values are in good agreement.

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