

## The effect of the calcination temperature of boehmite on its Co(II) adsorption properties

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The effect of the calcination temperature treatment of boehmite over its adsorption ability of Co(II) is presented. The materials obtained were characterized through their crystal structure, morphology, specific surface area, surface hydroxyl group content, and Co(II) adsorption at room temperature. It was found that a maximum cobalt adsorption capacity of  $1.6634 \times 10^{-3}$  meq  $\text{Co}^{2+} \cdot \text{g}^{-1}$  in boehmite calcined at 673 K, which showed the highest values of specific surface area and surface hydroxyl group content compared with the other boehmite samples. The specific surface area of boehmite samples became narrow when the calcination temperature was increased, and the cobalt ion adsorption onto boehmite depends on the specific surface area, but it depends mainly on the transition state of alumina because hydroxyl groups are regenerated on the surface of boehmite when the material is suspended in water; therefore, the calcined boehmite is suitable for cobalt adsorption.

**Key words:** Boehmite, Cobalt ion, Adsorption, XRD.

### Introduction

Industrial wastewater often contains heavy metal ions that could cause water pollution. Thus, several treatment methods have been used for the removal of heavy metal ions from water. In this way, adsorption can be used for the removal of toxic heavy metals from wastewater. Several solids have been used as adsorbent materials: activated carbons, zeolites, metallic oxides, and clays. Recent studies have recognized the importance of the ion adsorption properties of boehmite, as it is the most common aluminum oxyhydroxide mineral in nature [1-4]. Recently, boehmite has been used for the removal of Cr(VI) from aqueous solution [5]. It is generally accepted that boehmite (AlOOH) is an important precursor for various advanced transition materials, such as  $\gamma\text{-Al}_2\text{O}_3$ , which are widely used in the refining industry as a catalyst support [6] and membranes due to their high specific area and mesoporous properties and the fact that they are compounds that may be synthesized by the sol-gel method [7] via precipitation in ethanol [6], hydrolysis of alumina alkoxide [8], or neutralization of aluminum salt solutions [9]. Aluminum hydroxides are the hydrated precursors of transition aluminas. The dehydration process is mainly determined by the structure of the precursor. For instance, starting from the boehmite precursor, the dehydration process leads to the stable  $\alpha$ -alumina phase (corundum) via a great variety of metastable structures

of transition aluminas, including  $\gamma$ -phase,  $\eta$ -phase,  $\delta$ -phase, and  $\theta\text{-Al}_2\text{O}_3$ , which have enormous technological and industrial applications. The crystalline structure of boehmite has an essential effect on the characteristics of transition aluminas and the phase transition temperature of aluminas [10]. The structure of all transition aluminas is based on a face-centered cubic (*fcc*) array of oxygen anions [11], so the structural differences between these forms only involve the arrangement of aluminum cations in the interstices of the face-centered cubic array of the oxygen anions. Boehmite was thought to exist in two distinct forms, well-crystallized boehmite and pseudo-boehmite, with significantly different morphologies, porosity, and specific surface areas, but it was found that pseudoboehmite is simply micro-, or, rather, nano-crystallized boehmite [10]. Therefore, control of the calcination temperature is essential for materials that pass through transitional state forms to prove changes in the crystal system. As a result, the specific surface area and surface hydroxyl group content of the material decreases or increases as a function of the calcination temperature. For instance, porous materials present nanopores or surface active sites which could be determining in adsorption processes. The specific surface area or the pore size distributions are, with morphology, some of the parameters that condition reactivity, electrochemical and catalytic activities, and the molecular sieve effect.

On the other hand, cobalt has both beneficial and detrimental effects for health; it is beneficial to human beings because it comprises the B12 vitamin, but exhibition at high cobalt levels can produce negative effects on humans. In addition, it has been determined that cobalt and its compounds are carcinogenic [12]. Cobalt is an important

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radioactive liquid byproduct of nuclear technology. Its main radioisotopes are used in many applications in radiology and medicine.  $^{60}\text{Co}$  is an important element derived from nuclear processes, has a radioactive lifetime of 5.3 years, and is a pure gamma energy emitter; thus, it is important to retain and separate it from water [13]. Indeed, cobalt retention is, now, well understood [14-17]. Regarding this, recent studies have recognized the importance of the ion adsorption properties of boehmite; however, at present, there are few studies on the removal of aqueous metal cations with boehmite [18-20], and there has been no report about the relationship between the calcination temperature of boehmite and its adsorption ability for cobalt ions from aqueous solution.

In this study, the relationship between the calcination temperature of boehmite and its adsorption ability for cobalt ions from an aqueous solution is presented, based on the results of X-ray diffraction (XRD), specific surface area, and surface hydroxyl group content of boehmite obtained at different calcination temperatures.

## Materials and Methods

All chemical reagents used in this study were of analytical quality, and de-ionized water was used for the preparation, dilution, and analytical purposes of solutions. A stock solution of Co(II) was prepared by dissolving  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99.9% Aldrich) in deionized water. Cobalt concentrations in the remaining solutions were determined using a Shimadzu ultraviolet-visible 265 spectrophotometer analyzer at  $\lambda = 511 \text{ nm}$ .

Boehmite was synthesized via the sol-gel method at 298 K by the drop-wise addition of an isopropanol and water mixture under vigorous stirring in 100 ml of  $0.5 \text{ mol}\cdot\text{l}^{-1}$  aluminum isopropoxide/isopropanol solution for 24 h to obtain homogenization. For complete hydrolyzation, the mixture was heated in a reflux system at 328 K for 5 h. The solid obtained was filtered and washed with deionized water and then dried at 353 K [21].

For the calcination treatment, boehmite powders with different crystallinities were synthesized by heating boehmite powder obtained by the sol-gel method in an ambient atmosphere at the appropriate temperature (ranging from 473-1273 K) in a porcelain crucible, which was placed into a muffle furnace for two hours.

A Siemens D-5000 diffractometer coupled to a copper anode tube was used to obtain the X-ray diffraction (XRD) patterns and identify the crystalline compounds in each sample. The  $\text{K}_\alpha$  wavelength was selected with a diffracted beam monochromator. The morphology was determined using a scanning electron microscope (SEM) (Philips XL-30), and specific surface areas were obtained through standard multipoint techniques of nitrogen adsorption through the BET method with a specific area analyzer (Micromeritics Gemini 2360). The surface hydroxyl group content was determined by the fluoride-reaction method [22].

Batch Co(II) adsorption experiments using boehmite

samples were carried out at room temperature and mixing, in closed vials, 0.1 g of each boehmite sample and 10 ml of a  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$   $1 \times 10^{-2} \text{ mol}\cdot\text{l}^{-1}$  solution at pH 5.4. Samples were stirred for 10 s and shaken for 2 h. The liquids were separated from the solids by centrifugation (5 minutes at 3000 rpm), and 5 ml portions of liquid phases were taken off for cobalt measurements. The amount of  $\text{Co}^{2+}$  adsorbed at time ( $q$ ) was calculated using the following equation:

$$q = (C_o - C_f)V/m \quad (1)$$

where  $C_o$  is the initial cobalt concentration ( $\text{mg}\cdot\text{l}^{-1}$ ),  $C_f$  is the final cobalt concentration ( $\text{mg}\cdot\text{l}^{-1}$ ),  $m$  is the mass of calcined boehmite (g), and  $V$  is the solution volume (l). The pH of the supernatant measured at the end of the experiments was assumed to be the equilibrium pH; as a result, pH (~5.4) was increased after adsorption (6.4) in all boehmite samples as compared with that of the cobalt solution before adsorption.

## Results and Discussion

In Fig. 1, the X-ray diffraction patterns of the boehmite samples after calcination treatment are compared to the pattern of the boehmite as prepared by the sol-gel method. Fig. 1(a) shows a typical boehmite-type pattern when the compound was identified by making a comparison with the JCPDS 83-2384 card in the conventional way, where it is clear that all the sharp and not well-defined peaks correspond to the pure and non-crystalline phase of boehmite and no peaks of impurities were detected. The XRD analysis indicated that the boehmite powder exhibited extensively

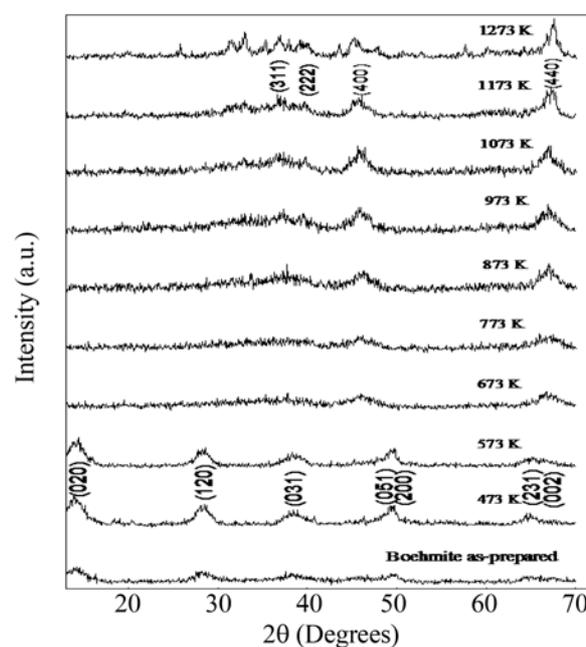


Fig. 1. XRD of boehmite samples thermally treated at different temperatures.

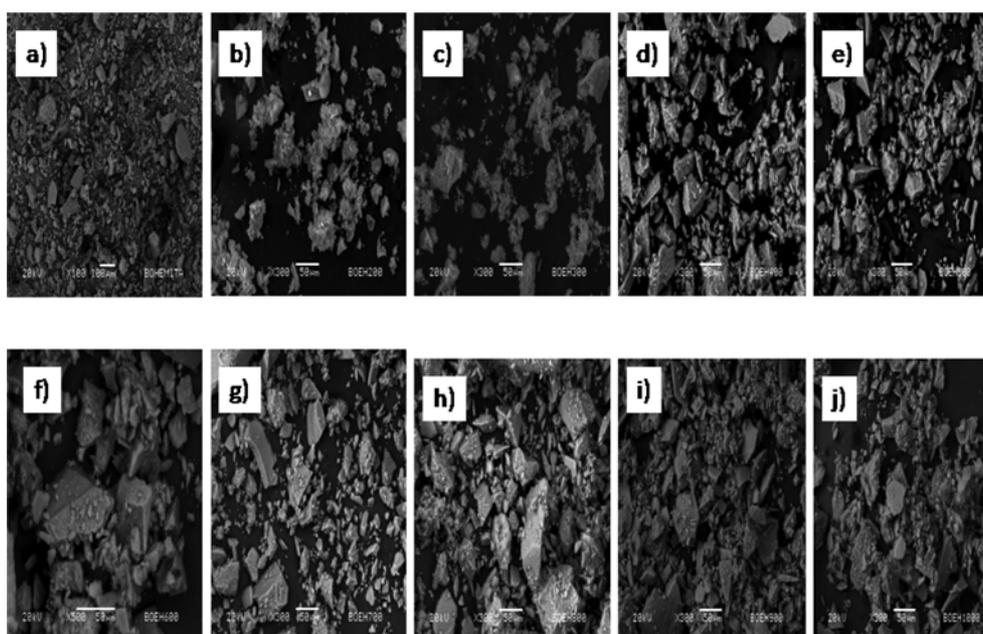
broadening reflections; Lu *et al.*, [9] reported that this means that the boehmite powders contain extremely small boehmite crystallites in addition to the existence of an amorphous phase. The powder diffraction pattern of the calcined boehmite after cobalt adsorption did not show any important changes; therefore, the crystal structure was confirmed by powder X-ray diffraction. Fig. 1 also shows the XRD patterns of the solids after heating at the temperatures studied (calcined boehmite samples). A broader shoulder between  $2\theta = 15^\circ$  and  $2\theta = 25^\circ$  together with poor crystallized signals due to AlOOH was detected from the solids, while semi-crystallized patterns were detected from the solids heated to high temperatures at around 673 K. We observed that, upon heating to  $> 673$  K, the boehmite structure can be destroyed and aluminum oxide can be generated; then, when the boehmite powder was calcined at 773 K for 2 h, it was completely converted to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, as confirmed by XRD analysis. Hence, all of the synthesized materials treated at temperatures higher than 773 K consist of a non-crystalline compound (Al<sub>2</sub>O<sub>3</sub>); only the boehmite treated above 1273 K were fully crystalline. When the calcination temperature was increased, aluminum oxide passed in a variety of metastable structures through transitional states ( $\gamma$ -form to  $\theta$ -form), finally becoming stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Therefore, the results of the X-ray diffraction showed that the structure of the boehmite changed drastically at temperatures of 473 to 673 K and 1173 to 1273 K; these results were previously observed by Kawasaki *et al.* [23], and they determined by differential thermoanalysis that an endothermic reaction and changes in the aluminum oxide structure occurred near a calcined temperature of 573 K. The XRD patterns found in this study are in accordance with the structural evolution of the phases and in agreement with previous studies on alumina [24, 25].

To achieve the purpose of the present study, alumina phases were obtained by heating oxyhydroxide AlOOH (boehmite) at different temperatures. It has been established using XDR and IR spectroscopy techniques that the boehmite is transformed by calcination treatment into the most stable phase of alumina,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, via the sequence of the  $\gamma$ ,  $\delta$ ,  $\theta$ , and  $\alpha$  phases [26, 27]. This polymorphism can be classified in terms of the oxygen sublattice structure and the distribution into this sublattice of aluminum ions in tetrahedral and octahedral interstitial sites. Thus, in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, the oxygen sublattice is a hexagonal, close-packed (*hcp*) structure with 2/3 of octahedral sites occupied with cations, while  $\gamma$ ,  $\delta$ , and  $\theta$  have a face-centred cubic (*fcc*) arrangement of oxygen atoms and cations present in various proportions in both octahedral and tetrahedral sites [27]. Phase transitions induced by heat treatment of boehmite [25] have established that boehmite crystallizes as orthorhombic cells and is composed of AlOOH sheets piling up with the oxygen ions located either in the sheets (O<sub>I</sub>) or at their surface (O<sub>II</sub>). The aluminum ions located in the center of octahedral sites are surrounded by 4 O<sub>I</sub> and 2 O<sub>II</sub>, and OH groups bound to the octahedron double

layers [28]. During the dehydration of boehmite, the spinel structured  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> develops first. The initial boehmite orthorhombic structure evolves, with the *c* parameter decreasing, while the *fcc* structure of the anionic sublattice remains. The octahedral Al<sup>3+</sup> ions are ordered, while the tetrahedral Al<sup>3+</sup> ions are disordered and anisotropic, leading to a distortion of the tetrahedron. As a result of this investigation, good agreement between the XRD pattern obtained on boehmite samples is maintained at 573 K after 2 h of heating (see Fig. 1), but  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> appears (JCPDS 10-0425) and only the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase is present above this temperature. For samples prepared at intermediate temperatures (473 to 1273 K), none of the XRD pattern reported in Fig. 1 is specific to a pure crystalline alumina phase. Instead, the comparison with reference patterns shows dominant  $\gamma$ ,  $\delta$  (46-1131 JCPDS card), and  $\theta$  (35-0121 JCPDS card) phases.  $\theta$ -Al<sub>2</sub>O<sub>3</sub> has a monoclinic structure that is isomorphic with  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> with the oxygen atom distribution close to a *fcc* lattice and the cations distributed in equal numbers on the octahedral and tetrahedral sites. Therefore, the  $\gamma$ ,  $\delta$ , and  $\theta$  transformations are accompanied by the Al<sup>3+</sup> migration from the octahedral to the tetrahedral sites, with the *fcc* oxygen sublattice being preserved. Thus, when heating up boehmite, all OH are eliminated, and various metastable transition aluminas are formed, principally the  $\gamma$  and  $\delta$  phases, to finally reach the  $\theta$ -Al<sub>2</sub>O<sub>3</sub> phase; however, in this investigation, boehmite was calcined only up to 1273 K, and it was not possible to obtain the most stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase, which can be obtained from boehmite at temperatures of 1423-1473 K [29]. On the other hand, the transformation of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> into  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is associated with the migration of ions in both sublattices. The oxygen ion sublattice is modified from an *fcc* to a hexagonal one; meanwhile, tetrahedral Al<sup>3+</sup> ions are no longer present in  $\alpha$  alumina and only AlO<sub>6</sub> units are present.

The changes in the crystal system were almost the same as the results generally observed in the calcination of aluminum oxide; the formation of transition alumina through various heat treatments has been evidenced and the transformation in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> studied [30]. The heating of boehmite or gibbsite at over 1273 K yields a variety of transition aluminas before the stable corundum is formed [31]. Additionally, in recent publications [32, 33], it has been shown that the well-known temperature-induced transition from boehmite ( $\gamma$ -AlOOH) to corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) occurs from  $> 623$  K to  $> 1473$  K. The transition temperatures are somewhat approximate, but it is worth remembering that, although all transition aluminas are stable at room temperature, they are normally activated only at the temperatures indicated above and cannot be retracted in reverse with decreasing temperature.

The size and shape of the grains among the boehmite samples prepared determined by SEM are not very different (Fig. 2). The particles of boehmite synthesized by the sol-gel method are large, irregular, layered, and close to 10-100  $\mu$ m. The particle surface is smooth and typical of a not well-crystallized material.



**Fig. 2.** Top-view SEM images of the boehmite samples thermally treated at different temperatures: a) boehmite, b) 473 K, c) 573 K, d) 673 K, e) 773 K, f) 873 K, g) 973 K, h) 1073 K, i) 1173 K, and j) 1273 K.

The specific surface areas of boehmite heated at different temperatures show an increase at the calcination temperature of 773 K, reach a maximum at a calcination temperature of 673 K, and then decrease as the calcination temperature rises (Table 1). When the calcination temperatures were controlled between 473 and 1273 K, amorphous and crystalline aluminas with specific surface areas of  $222.9 \text{ m}^2 \cdot \text{g}^{-1}$  to  $92.9 \text{ m}^2 \cdot \text{g}^{-1}$  were found, respectively. A variation in calcination temperature of 800 K (from 473 to 1273 K) diminishes the specific surface area by more than 41.6%; therefore, the calcination temperature was essential in obtaining high or low specific areas. Boehmite heated at 1273 K showed a very low specific area of  $92.9 \text{ m}^2 \cdot \text{g}^{-1}$  due to the clustering of surface water, but powder of

boehmite heated at 573 K had a specific area of  $222.9 \text{ m}^2 \cdot \text{g}^{-1}$ , indicating a highly porous structure consisting of fine crystallites. The decrease in specific surface area with an increase in calcination temperature is due to the formation of a thermodynamically-stable structure (transitional phase formation); when the calcination temperature increased, the phase changed from amorphous to a metastable structure and then, finally, to the stable  $\alpha$ -alumina phase, undoubtedly accompanied by a decrease in specific surface area [34, 35]. Furthermore, our results have certain similarities with those reported by Hitetale *et al.*, [36] in silica-aluminum gel. Therefore, the results showed that the calcination temperature was the major factor in determining the specific surface area and the phase composition of the final product. On the other hand, the main reason for the efficient metal adsorption capacity on the surface of any adsorbent material is thought to be the presence of surface hydroxyl groups, which determine the extent to which metal ions in aqueous solution are bonded to the surface as active sites that are able to remove pollutants from water. Instead, in this study, the number of hydroxyl groups was postulated to measure the cobalt adsorption capacity of the calcined boehmite samples. The results show that the number of surface hydroxyl groups of the calcined boehmite samples was the highest when the calcination temperature was 673 K; a maximum number of surface hydroxyl groups of  $6.76 \text{ mmol} \cdot \text{g}^{-1}$  was found. Above 673 K, the number decreased with increasing calcination temperature; this loss is due to the dehydration and dehydroxilation of the samples, which are significantly reduced at higher temperatures, thus inhibiting the presence of surface hydroxyl groups. The boehmite contained adsorbed water on the grains and interlayer water in the crystal structure; furthermore,

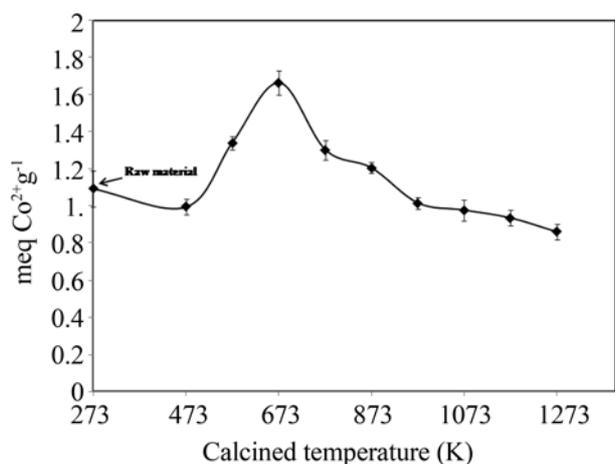
**Table 1.** Specific surface area, amount of hydroxyl group of boehmite and calcined boehmite samples treated at different temperatures

Calcination temperature (K)	Specific surface area ( $\text{m}^2 \text{ g}^{-1}$ )	Amount of hydroxyl group ( $\text{mmol g}^{-1}$ )
untreated	254.3	3.02
473	222.7	3.45
573	222.9	5.16
673	237.4	6.76
773	237.1	5.37
873	203.3	4.32
973	188.2	4.26
1073	160.5	3.77
1173	130.5	3.66
1273	92.9	1.51

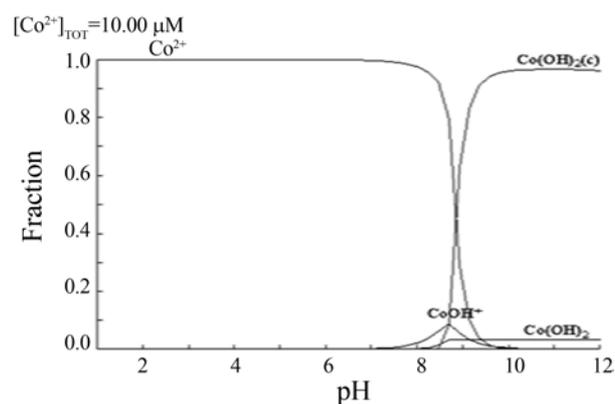
hydroxyl groups were also reported in the crystal structure of the boehmite and transition aluminas, one of which dehydrates during the conversion of boehmite into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at around 773 K, while another remains in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, being gradually lost upon heating. A study of the phase transition of boehmite powders examined by differential thermal and thermogravimetric analysis (DTA-TGA) reported by Lu *et al.*, [9] reveals that the weight loss of crystalline boehmite powder below 460 K corresponds to the desorption of adsorbed water, while the weight loss occurs between 513 and 883 K due to the dehydration of the interlayer water and the decomposition of the hydroxyl groups in the crystal structure of the boehmite and aluminum oxides.

The amount of retained cobalt (II) ions in the boehmite and calcined boehmite samples is shown in Fig. 3. The values of meq·g<sup>-1</sup> vary from  $0.8604 \times 10^{-3}$  to  $1.6634 \times 10^{-3}$ , with the highest value corresponding to the sample heated at 673 K. The morphological features of those materials are rather similar, and specific surface areas decrease above 773 K, so only the external textural surface characteristics of the particles shows a dependence with Co(II) adsorption.

It is possible that the efficiency of cobalt adsorption on the calcined boehmite can be due to different factors, such as the specific surface area and hydroxyl group content of the adsorbent or the concentration and type of the chemical species present of the adsorbate in the aqueous solution. According to the chemical equilibrium diagram for cobalt speciation [37], the hydrolysis products of the Co<sup>2+</sup> ions (Fig. 4) appear to have pH values inferior to 9 and interact with the surface because these materials acquire an electrical charge through reactions that involve functional groups (H<sup>+</sup>, OH<sup>-</sup>) on the surface of the mineral and the ions present in the solution; this type of charge is variable and depends considerably on the pH of the solution. The cation adsorption on the surface of the boehmite will, therefore, be favorable to alkaline pH values and the

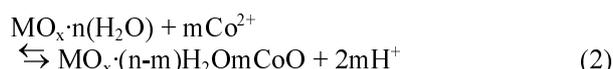


**Fig. 3.** Co(II) adsorption on boehmite and calcined boehmite samples. Experimental conditions: concentration of Co(II) =  $1 \times 10^{-2}$  M; equilibrium pH 6.4; room temperature.



**Fig. 4.** Cobalt chemical species in aqueous solution as a function of pH.

opposite for anions. These observations are consistent with previous investigations of ReO<sub>4</sub><sup>-</sup> anions adsorbed on boehmite [38] and organic anion adsorption on boehmite [39], such that the anion adsorption appears to be most effective at acid pH values. In this study, the cobalt adsorption process was made at equilibrium conditions; the pH of the solution after adsorption (equilibrium pH) was 6.4. The optimum pH value for the removal of Co(II) was found in alkaline pH aqueous solutions [14-17]. On the other hand, the hydroxyl groups present on the surface of the oxides allow the interaction of the chemical species in the solution due to attraction processes or the electrostatic repulsion of loads, which can be accompanied by a mechanism of ion exchange represented by the following general equation:



Experimentally, it has been established that the ion exchange that presents the metallic oxides hydrated as aluminas, due to the adsorbed water on the surface of particles in contact with this, creating a new surface, as suggested by Ogata *et al.*, [3], who reported that the arsenious removal on boehmite is due to the fact that the hydroxyl groups were first generated by the reaction of boehmite with water molecules in the metal solution, and then the hydroxyl groups were ion-exchanged with arsenious ions as a mechanism by which arsenious ions were adsorbed by calcined boehmite. Therefore, the boehmite structure is disrupted by the calcination of boehmite and changed to a compound having an aluminum oxide structure as a mechanism by which cobalt ions are adsorbed by boehmite. When calcined boehmite is suspended in deionized water, water molecules are desorbed and boehmite with a hydroxyl group on the surface is generated. This hydroxyl group is ion-exchanged with a cobalt ion, and then the cobalt ion in aqueous solution is adsorbed. Therefore, the results indicate that the adsorption mechanism of a cobalt ion

onto boehmite and calcined boehmite samples occurs by ion exchange with hydroxyl groups on the boehmite surface. The present results are in accordance with those reported by McBride, Kraemer *et al.*, and Hota *et al.*, [40-42], who suggested that ion exchange is the adsorption mechanism for the removal and regeneration of aqueous divalent cations, principally  $Pb^{2+}$ ,  $Cd^{2+}$ , and  $Cu^{2+}$ , by boehmite. The oxygen in the water connects with the metal, whereas the hydrogen in the water is exposed and interchanged by the metallic ions of the solution.

Since surface reactivity and the adsorption properties of solids are important factors in controlling the transport of toxic and radioactive elements in water and porous media, one should take into account the stability of solids, especially of their surfaces. Therefore, the results indicate that boehmite, a solid rich in aluminates with a low cost and without pollution, may be useful in the removal of pollutants in water specifically cobalt with good results.

### Conclusions

The study of various calcined boehmite phases has shown that initial approaches are accurate at solid phases involving  $Co^{2+}$  adsorption. The calcination process has an important influence on the surface reactivity of boehmite and, hence, on its adsorption properties. The decrease in the density of sites to chemical species is essentially explained by the low reactivity of the surface hydroxyl groups of boehmite via a calcined step corresponding to an amorphous or crystalline phase. The morphology of the samples does not depend on the temperature used for the synthesis; large, irregular, layered particles and porous particles can be observed. Although the specific surface area of boehmite becomes narrow with an increase in the calcination temperature, the amount of cobalt ions adsorbed onto boehmite depends on the specific surface area and the transition state of alumina due to the fact that the hydroxyl groups are regenerated on the surface of boehmite when the material is suspended in water. Therefore, more hydroxyl groups on the surface retained more cobalt ions. Hence, the material treated at 673 K (specific area :  $237.4 \text{ m}^2 \cdot \text{g}^{-1}$ ; morphology : lamellar and porous; hydroxyl groups :  $6.76 \text{ mmol} \cdot \text{g}^{-1}$ ) presented the best performance in  $Co^{2+}$  retention. This approach could be usefully generalized to other families of hydroxides (iron and manganese) that are naturally abundant and present various interests.

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