Surface Complexation of Chromium(VI) on Iron(III) Hydroxide: Mechanisms and Stability Constants of Surfaces Complexes

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Abstract: *The adsorption of chromate ions $H_{2-y}A$ (y = 1, 2, and A = CrO_4^{2-}) on iron(III) hydroxide was conducted as a function of adsorbent mass, solution pH, and hydration time. The surface complexation technique, based on the examination of the chromate distribution between the solid and liquid phases, was adopted to predict the adsorption mechanism. To specify stoichiometry of the chromate surface complexes, the proton ($n > 0$) and hydroxyl ($n < 0$) ion-exchange was evaluated at a pH range of 2–12. The obtained "n" values are ranging between -1 and 1. As a result, the sorption process involved specific chemical interaction with surface sites, resulting in $1H^+$ and $1OH^-$ the adsorbate molecule's release. The surface species identified were $\overline{>S(OH_2^+)(HA^-)}$; $\overline{>S(OH_2^+)(A^{2-})}$; $\overline{>S(OH_2^+)(H_1A^{-1})}$; $\overline{>S(OH_2^+)(A^{2-})}$; $\overline{>S(OH_1^0)(A^{2-})}$; $\overline{>(SOH_2^+)-(H_1A)H_{-1}-S^{(-2)}}$; $\overline{>(SOH_2^+)-AH_{-1}-S^{(-1)}}$; $\overline{>S(OH)(A^{2-})}$ and $\overline{>(SOH_2^+-A-SOH)^{4-}}$. The logarithmic values of their complexing constants were: log K_{00} = 1.81 ± 0.04; log K_{11} = -3.53 ± 0.07; log K_{21} = -1.03 ± 0.23, log K_{1-1} = 7.15 ± 0.14 and log K_{2-1} = 9.62 ± 0.53. The results showed that the chromate adsorption on Fe(III) hydroxide was of electrostatic and chemical nature at pH lower than 5.5, and only of chemical nature at pH superior to 5.5. Therefore, Fe(III) hydroxide could be considered an excellent sorbent for removing Cr(VI) from wastewater solutions.*

Keywords: *chromium(VI); iron(III) hydroxide; adsorption; surface complexes; stability constants*

INTRODUCTION

Chromium is widely used in many industrial fields such as tanning, painting, dyeing ceramics, wood treatment, and the paper industry. These Industrial activities generate substantial amounts of hazardous wastes containing high concentrations of chromium [1]. The hexavalent chromium has been considered one of the most toxic pollutants because of its mutagenic, carcinogenic, and teratogenic properties in humans [2-6]. This element's discharge in the surface water is a severe threat to rivers, streams, and aquatic life. The presence of this metal is well controlled and the maximal concentration level of Cr(VI) allowed in drinking water, as determined by the US-Environmental Protection Agency (EPA), is 0.05 mg/L [7]. As a result, raising public concerns about environmental pollution requires sustainable technologies for reducing the chromium ions in wastewater to an acceptable level. Wastewater discharge of the Cr(VI) industry is largely treated using different adsorbents to meet environmental regulation [8-13]. However, this process and subsequent treatments have high operating costs. Accordingly, wastewater is still a managing difficulty for Cr(VI).

For this purpose, methods have already been developed, such, ion exchange [14], solvent extraction [15], precipitation [16-17], and adsorption [18-21]. These techniques are usually performed using conventional or non-conventional adsorbents, especially, zeolites, and iron(III) hydroxide [22-25]. However, adsorption is a technique of choice for the removal of dissolved elements as Cr(VI) from aqueous solutions. One can note that this procedure is often carried out using activated carbon [26-27], metal-organic frameworks [28-29], polymeric, and biomass materials [30-35]. A new study is recently conducted on hexavalent chromium adsorption and removal from the aqueous environment using chemically functionalized amorphous and mesoporous silica nanoparticles [36]. Nevertheless, iron oxyhydroxide or ferric oxyhydroxide (FeO(OH)), which has low solubility in water and often poorly crystalline, has a large surface area and more active sites for Cr(VI) adsorption.

The relevant reported functional groups of Fe(III) oxyhydroxide rich in defects are Fe–O, Fe–OH, and Fe–O–Fe [37]. Thus, FeO(OH) suspension develops surface charge (Q) due to the exchange of H^+ or OH^- ions resulting from the dissociation of hydration water molecules [38]. This exchange phenomenon's contribution to Q depends on the transfer of proton to hydroxo complex interface $(\overline{>SOH})$, which is a function of the medium suspension acidity [39]. As discussed previously, the proton transfer reaction can be treated as an acid-base equilibrium after protonation/deprotonation of $\overline{>SOH}$ [40].

This study's mean objective consists of surface complexation of hexavalent chromium ions on iron(III) hydroxide. For this purpose, the sorption of Cr(VI) is examined through co-precipitation experiments from aqueous solution, as a function of contact time, the mass of adsorbent, and equilibrium pH of chromium solution 10^{-5} M. The ion exchange method, which has already been successfully used in liquid-liquid extraction, is carried out, in order to examine the sorption and the complexation of ions chromates with the surface of amorphous $Fe(OH)_3{\cdot}xH_2O$.

■ EXPERIMENTAL SECTION

Materials

Chemicals namely potassium dichromate ($K_2Cr_2O_7$, 99%), sodium hydroxide (NaOH, 99%), potassium permanganate ($KMnO_4$), iron(III) chloride ($FeCl_3$, 99%), and nitric acid (HNO_3, 99%) were used and purchased from Sigma Aldrich. The reagents are of analytical grade and used without further purification [41]. High quality distilled water is used for all the experiments.

Instrumentation

The equipment used in this research was a magnetic stirrer, laboratory balance ADB, KERN of precision 10^{-4} g, and MIKRO 200 HETTICH benchtop centrifuge. The pH of sample solutions was measured using a METROHM pH-meter of precision 10^{-3} pH unit, equipped with a previously calibrated double concentric electrode. Analysis of the dosage of chromium(VI) is carried out in the aqueous phases before and after adsorption by a GBC type 902 UV-Visible spectrophotometer.

Procedure

The adsorption studies are carried out by co-precipitation of $Fe(OH)_3$. The iron(III) masses used in this case are 60, 100, and 300 mg/L, while the contact time is varied in the range of 1–24 h. Co-precipitation experiments are examined using a 10^{-5} M solution of potassium permanganate. The pH is adjusted by decimolar solutions of NaOH or HNO_3. Chromium co-precipitation is carried out with 100 ml of amorphous ferric oxyhydroxide solution at various pH and Fe^{3+} concentrations.

The co-precipitation efficiency is determined using the ratio of Cr(VI) concentrations in solid and aqueous phases, which corresponds to the partition coefficient (D). The concentration of hexavalent chromium is measured in the aqueous phase by using a UV-Visible spectrophotometry technique.

Adsorption experiments

The dosage of chromium in the aqueous solution is carried out by UV-Visible spectrophotometry technique. For this purpose, 0.2 mL of the 1,5-diphenyl-carbazide complexing agent is acidified with 4 mL of 0.05 M sulfuric acid solution and completed to 5 mL with distilled water. The co-precipitation of chromium ions by the $Fe(OH)_3$ is examined according to the contact time, the pH of the suspension, and the mass of the iron hydroxide. The effect of pH on the partition of Cr(VI) between the solution and the solid phase is examined for various contact times.

The effect of pH and mass of sorbent on Cr(VI) sorption is described by Eq. (1).

$$\log D = \log K_{ap} + \log m + npH \qquad (1)$$

$$D = \frac{\overline{[Cr(VI)]}}{[Cr(VI]} \qquad (2)$$

K_{ap} is adsorption constant, "m" is sorbent amount in g/L and the on lined species referrer to the solid phase. If "P" denotes the percentage of chromium fixation on iron(III) oxyhydroxide we obtain:

$$D = \frac{P}{1-P} \rightarrow P = \frac{D}{1+D} \qquad (3)$$

■ RESULTS AND DISCUSSION

Effect of pH

The experimental results of the adsorption of chromate ions on iron(III) hydroxide are given in Fig. 1, as a logarithmic variation of D with pH for iron contents equal to 60, 100, and 300 mg.L^{-1} at contact times (t_{ct}) of 0.5, 1, 2, 3, 4, and 26 h. One can note that these curves are to define the mechanisms of chromium adsorption involved in this case. Fig. 1 shows log D = f(pH) obtained for various contact times and suspension amounts.

In acidic media, log D = f(pH) variations are linear until reaching a maximum (P∽90%) at pH_{max} ranging from 5 to 6, then decrease rapidly when the pH continues to rise. It must be noted that at given "m," the values of both pH_{max} and δ log D/δ pH are dependent on the duration of adsorbent hydration. This indicates the absence of a predominant reaction and shows the absorption phenomenon's complexity, which seems to involve several reactions of fixation of Cr(VI) by iron hydroxide. According to the suspension medium's acidity, the variations in chromium(VI) retention with acidity are due to the protonation/deprotonation reaction of both chromic acid and sorbent surface groups $(\overline{>SOH})$. The first and second acidity constants of H_2CrO_4 are respectively $pK_{a1} = 0.75$ and $pK_{a2} = 6.45$ [42]. At concentrations lower than 0.03 M, Cr(VI) exists mainly as hydrogen chromate $HCrO_4^-$ at pH ≤ 5.0 (≥ 95%), chromate CrO_4^{2-} for pH ≥ 7.6 (95%), and as a

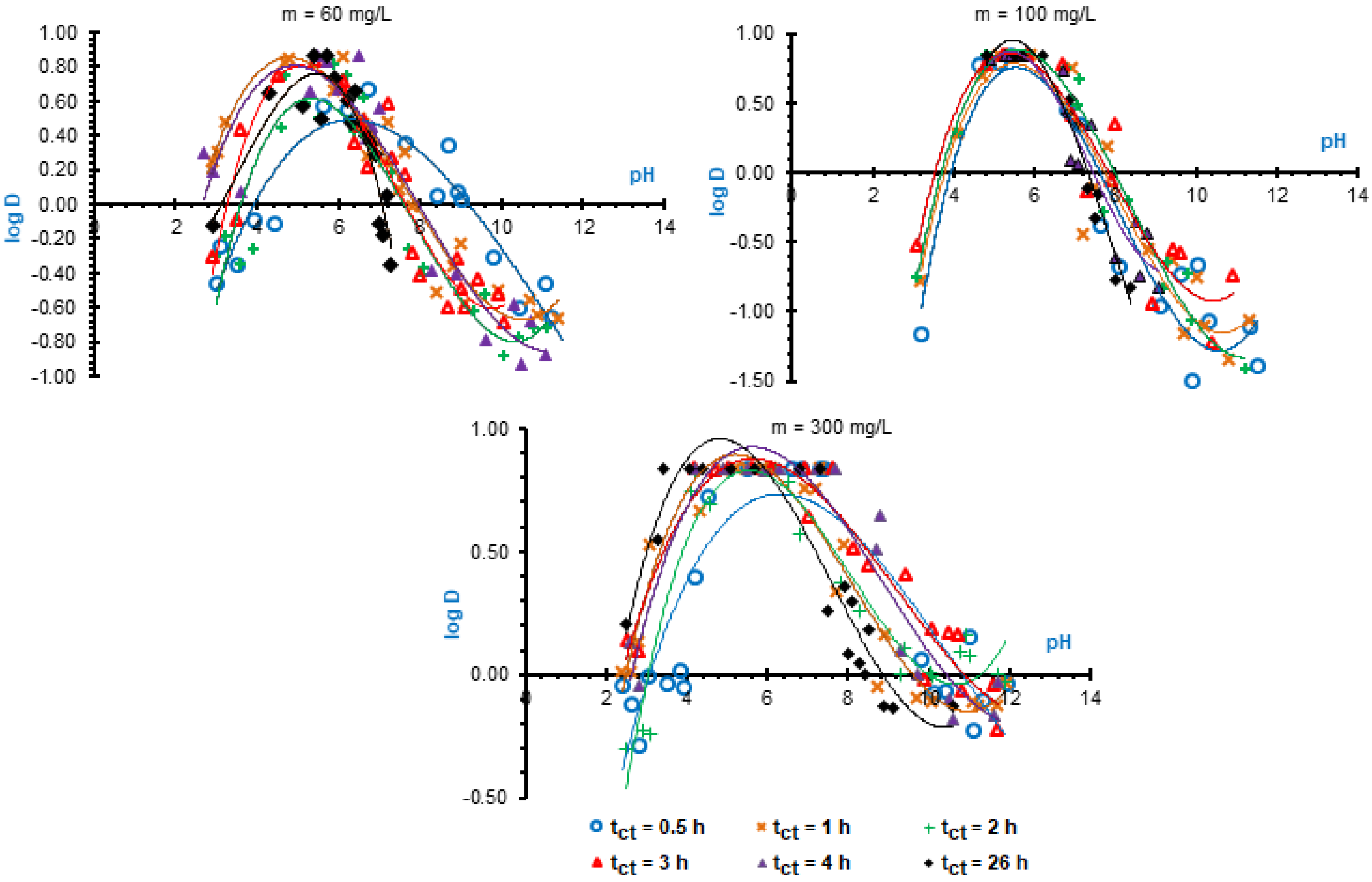

Fig 1. Log D versus pH for m = 60, 100, and 300 mg/L and contact times t_{ct} = 0.5, 1, 2, 3, 4, and 26 h

mixture of these two species between pH 5.0 and 7.6. Moreover, the electrostatic and chemical sorption mechanisms are very rapid, that the kinetics cannot be used to differentiate between these two processes [43].

The maximum adsorption conditions are exhibited when the surface charge of the sorbent is opposite to that of the sorbate. Thus, the binding of weak acids is maximal at pH values close to the pK_a of these acids or to the PZC of the surface absorbent materials [42-44]. Taking these considerations into account, H_2CrO_4 can be considered a strong diprotic acid dissociated into $HCrO_4^-$ and adsorbed electrostatically onto the positively charged hydroxide surface up to pH around PZC∽7. It is shown from previous studies that the adsorption of Cr(VI) is, in general, optimal at pH values lower than 4 for various absorbents such as some metal oxyhydroxides [45, 46], natural biosorbents such as larch bark [47], boiled tea leaves [48] and activated charcoal [49]. Also, optimum pH for adsorption of this metal ion is found to be ranging from 5 to 7 with various adsorbents such as clays [50], sands covered with oxides [50], zeolite and hydroxyapatite [51-52], aluminosilicate [50-53], apricot stone [54], bamboo waste [55] and seed-based biochar [56]. This acidity effect is considered to be due to the interaction of the surface sites $\overline{(>\mathrm{SOH})}$ that is much greater with H^+ ions than with sorbate anion. At pH greater than pH_{max}, Cr(VI) exhibits a typically anionic sorption behavior, and the adsorption decreases with increasing pH, as found in the retention of anions on iron oxides [57]. This behavior, usually observed at pH values higher than 6.0, is suggested to be due to the competition uptake of CrO_4^{2-} and OH^- anions by the surface of the adsorbent [58]. As a result, the obtained adsorption behavior involves the phenomena of protonation of the hydroxylated sites and the hydrolysis of chromium(VI). Thus, at pH higher than pH_{max}, the retention of Cr (VI) is due to the interaction of hydrogen chromate and/or chromate with $\overline{>\mathrm{SOH}}$ surface groups rather than with $\overline{>\mathrm{SOH}_2^+}$ groups that are predominating at pH below pH_{max} [59]. One can note that the non-integer values of $\frac{\partial \mathrm{logD}}{\partial \mathrm{pH}}$ =n is associated with two successive surface complexes [60].

Variation of $\frac{\partial \mathrm{logD}}{\partial \mathrm{pH}} = \mathrm{f(pH)}$

As shown below in Eq. (15), $\frac{\partial \mathrm{logD}}{\partial \mathrm{pH}} = \mathrm{n}$ corresponds to proton H^+ (n > 0) or hydroxyl OH^- (n < 0), exchanged during the surface complexation reaction described by Eq. (9). Obtained results show that the mechanism of Cr(VI) adsorption with $Fe(OH)_3$ sorbent occurs via electrostatic attraction or diffusion process ($\frac{\delta \mathrm{logD}}{\delta \mathrm{pH}} = 0$), proton ($\frac{\delta \mathrm{logD}}{\delta \mathrm{pH}} > 0$) and hydroxyl ($\frac{\delta \mathrm{logD}}{\delta \mathrm{pH}} < 0$) exchanges. In general, the adsorption phenomenon is a non-linear curve describing log D = f(pH) variations. To determine the "n" value, equilibrium adsorption data are best fitted with cubic polynomial equation ($R^2 > 0.99$), in various pH regions. Fig. 2 shows the variations n = f(pH) obtained for 60 mg/L ≤ m ≤ 300 mg/L, at contact times varying between 0.5 and 26 h.

These results demonstrate that the pH of the sorbent system controls the ionic forms of the chromium solutions and the surface properties of the adsorbent. In all the cases, the variations n = f(pH) exhibits a similar behavior that is varying significantly with the contact time, in particular in acid conditions. The protonation/deprotonation of the sorbent is dependent on the surface coverage and varies between -1 and 1 for m = 60, 100, and 300 mg/L. The protonation phenomenon is prevailing at pH around 2, while coulombic/intra-particle diffusion adsorption is predominantly for pH ranging from 4.4 to 6.0. Furthermore, the deprotonation is prevailing at a pH of around 8 in all examined media.

Combining these mechanisms leads to the predominance of surface complexes (C_{ln}), whose nature depends on the acidity of the aqueous medium. These species are C_{00}, C_{11}, C_{21}, $C_{1\text{-}1}$, and $C_{2\text{-}1}$. Taking these considerations into account, the predominant complexation reactions involved in this case are:

$$\overline{\mathrm{l}(>\mathrm{SOH})} + \mathrm{H_2CrO_4} \leftrightarrow \overline{(>\mathrm{SO})_l(\mathrm{H}_{2-2l}\mathrm{CrO}_{4-l})\mathrm{H}_{-n}^{(n-2)+}} + \mathrm{nH^+} + \mathrm{lH_2O} \quad (4)$$
$$\mathrm{n} = -1;1,\ \mathrm{l} = 1;2$$

$$\overline{\mathrm{l}(>\mathrm{SOH})} + \mathrm{H_2CrO_4} \leftrightarrow \overline{(>\mathrm{SO})_l(\mathrm{H}_{2-2l}\mathrm{CrO}_{4-l})\mathrm{H}_0} + \mathrm{lH_2O} \quad (5)$$
$$\mathrm{n} = 0,\ \mathrm{l} = 1;2$$

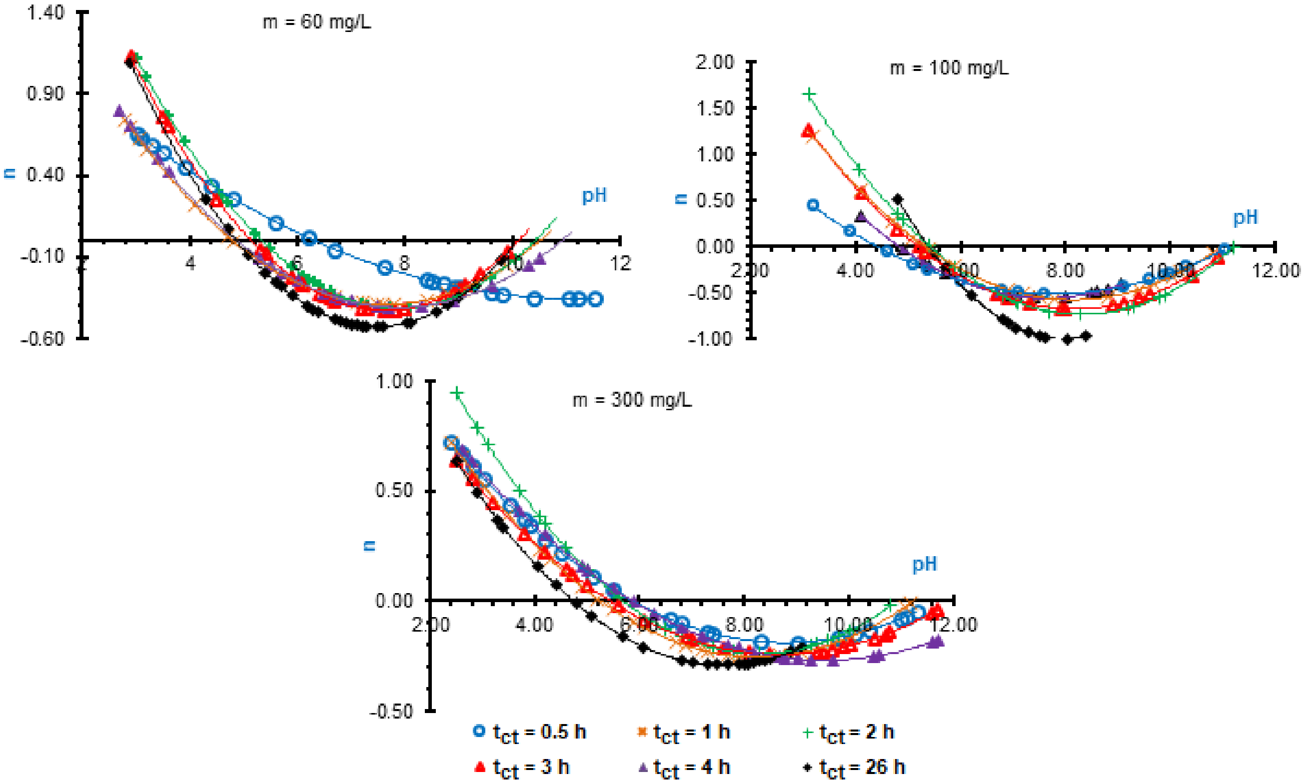

Fig 2. Variations of n = f(pH) obtained for m = 60, 100, and 300 mg/L at contact times t_{ct} = 0.5, 1, 2, 3, 4, and 26 h

Chromium(VI) Adsorption Mechanism and Stability Constants

In general, the process of adsorption of ion metal with hydrated oxyhydroxides is described by the complexation reaction of a metal ion with active sites $\overline{>S-OH}$. The acid-base properties of the surface of the adsorbents considered are attributed to the protonation/deprotonation reactions taking place on the surface of the sorbent and which can be expressed by:

$$\overline{(>S-OH)} + H^+ \leftrightarrow \overline{>S-OH_2}^+ \qquad K^+ \qquad (6)$$

$$\overline{(>S-OH)} \leftrightarrow \overline{>S-O^-} + H^+ \qquad K^- \qquad (7)$$

The highlighted species belong to the solid phase, so K^+ and K^- refer to the stability constants for iron(III) hydroxide.

The symbols H_{-1} and H_1 respectively denote the H atoms and the OH group. This leads therefore to:

$$H_{-1} + H_1 \leftrightarrow H_2O \qquad (8)$$

The surface complexation of chromium ions, $H_iCrO_4^{i-2}$, by Iron hydroxide can be described by the Sillen notation, generally adopted in complexing reactions in the aqueous phase.

$$l\,\overline{>SOH} + H_iA^{(i-2)+} \Leftrightarrow \overline{(>SOH)_l H_{(i-n)} A^{(i-n-2)+}} + nH^+ \quad K_{ln} \qquad (9)$$

with: i = 2; 1; 2, l = 1; 2, n = -1; 0; 1, and A = CrO_4^{2-}

Taking into account the expression of "D" given by:

$$D = \frac{\overline{\left|(>SOH)H_{i-n}A^{(i-n-2)+}\right|}}{\left|H_iA^{(i-2)+}\right|} \qquad (10)$$

The extraction constant is:

$$K_{ln} = \frac{\left|\overline{(>SOH)H_{i-n}A}\right|\left|H^+\right|^n}{\left|H_iA^{(i-2)+}\right|\left|>\overline{SOH}\right|^l} \qquad (11)$$

$$K_{ln} = \frac{\left|\overline{(>SOH)H_{i-n}A}\right|\left|H^+\right|^n}{\left|H_iA^{(i-2)+}\right|m^l} = \frac{D}{m^l}\left|H^+\right|^n \qquad (12)$$

where $\left|>\overline{SOH}\right| = m$

$$\log K_{ln} = \log D - l\ \log m - npH \qquad (13)$$

So that:

$$\log D = \log K_{ln} + l \log m + npH \quad (14)$$

According to these expressions, the study of the variation in the value of the distribution coefficient D as a function of pH makes it possible to verify the supposed binding mechanism and define the nature "n" of the adsorbed species calculate the K_{ln} constants.

$$\frac{\partial \log D}{\partial pH} = n \quad (15)$$

$$\frac{\partial \log D}{\partial \log m} = l \quad (16)$$

Study of Variations A_{ln} = l log m + log K_{ln} = f(n)

The surface complexation equilibrium constants are obtained from the line segments of the log D = f(pH) curves. The slope of these segments leads to the value of "n" while the y-intercept leads to A_{ln} = log K_{ln} + l log m. Fig. 3 illustrates the variations A_{ln} = f(n) for the successive contents of 60, 100, and 300 mg/L.

As shown, these variations are linear throughout the range of "n" explored. They allow the calculation of A_{l1}; A_{l0} and A_{l-1} relating to the various iron concentrations. So, the curve equation can be written in the form log (A_{ln}) = log (A_{l0}) + n log (A_n-A_{l0}). This equation can be obtained thermodynamically by considering that |n| also presents the fraction of the 1 H^+ or 1 OH^- exchange reaction, contributing to the overall adsorption reaction.

Study of the "l" Order of Surface Complexes

The ordinate at the origin of the variations log D = f(pH) is equal to A_{ln} = l log m + log K_{ln}. The exam of the variations A_{ln} = f(log m) for n = 1; 0 and -1 (Fig. 4) make it possible to determine "l " and logK_{ln}.

Fig. 4 shows that the graphs A_{ln} = f(log m) are linear whose slope values correspond to the "l" parameter.

As a result, the adsorption process combines mononuclear and binuclear uptake mechanisms. Accordingly, the surface complexation constants are log $K_{1.1,1}$ = -3.28, and log $K_{l.3,-1}$ = 7.89. As shown, A_{l0} = log K_{10} are constants, indicating that the intrinsic reaction is no dependent on suspension amount. This means that this steeper Cr(VI) adsorption is, essentially, controlled by film diffusion. One can note that this external surface sorption is characterized by l = 0, in these conditions. The logarithmic variation of K_{1n} associated with different monodentate complexes resulting from surface

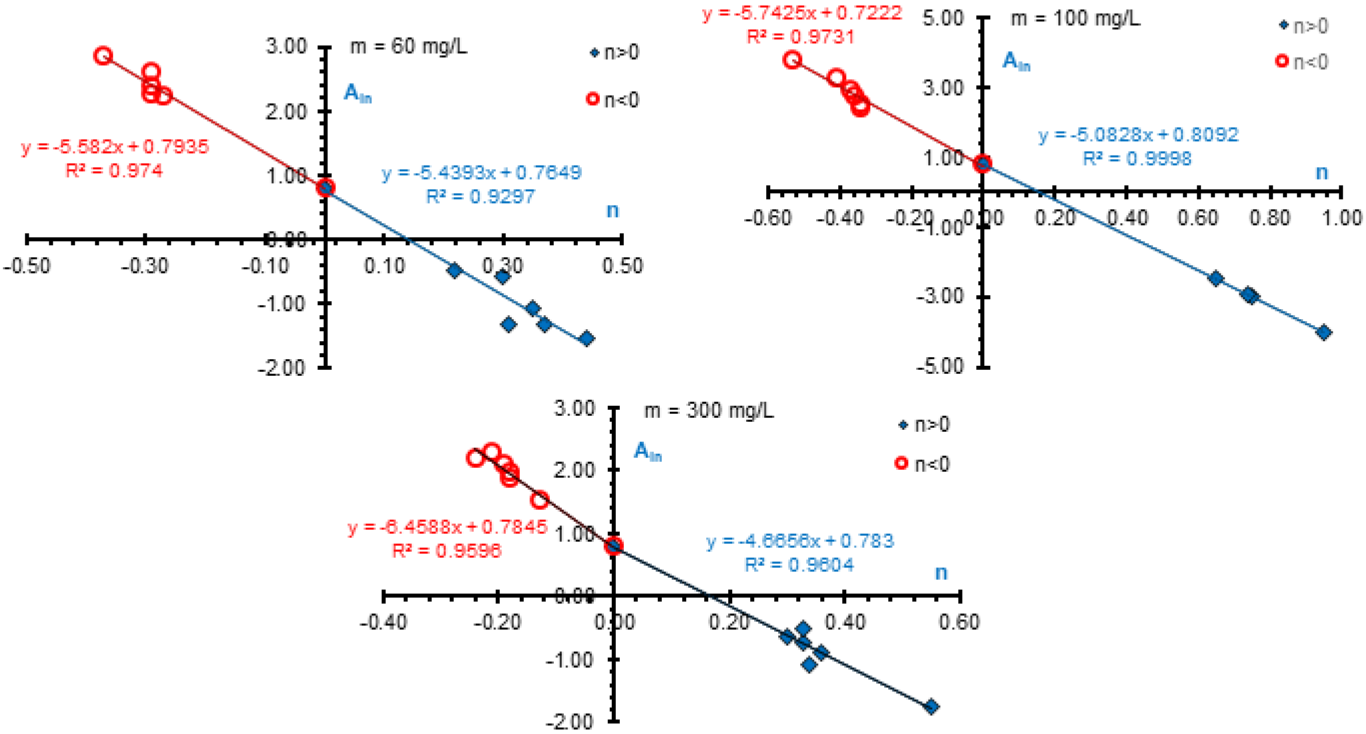

Fig 3. Variations of A_{ln} = f(n) obtained for m = 60, 100, and 300 mg/L

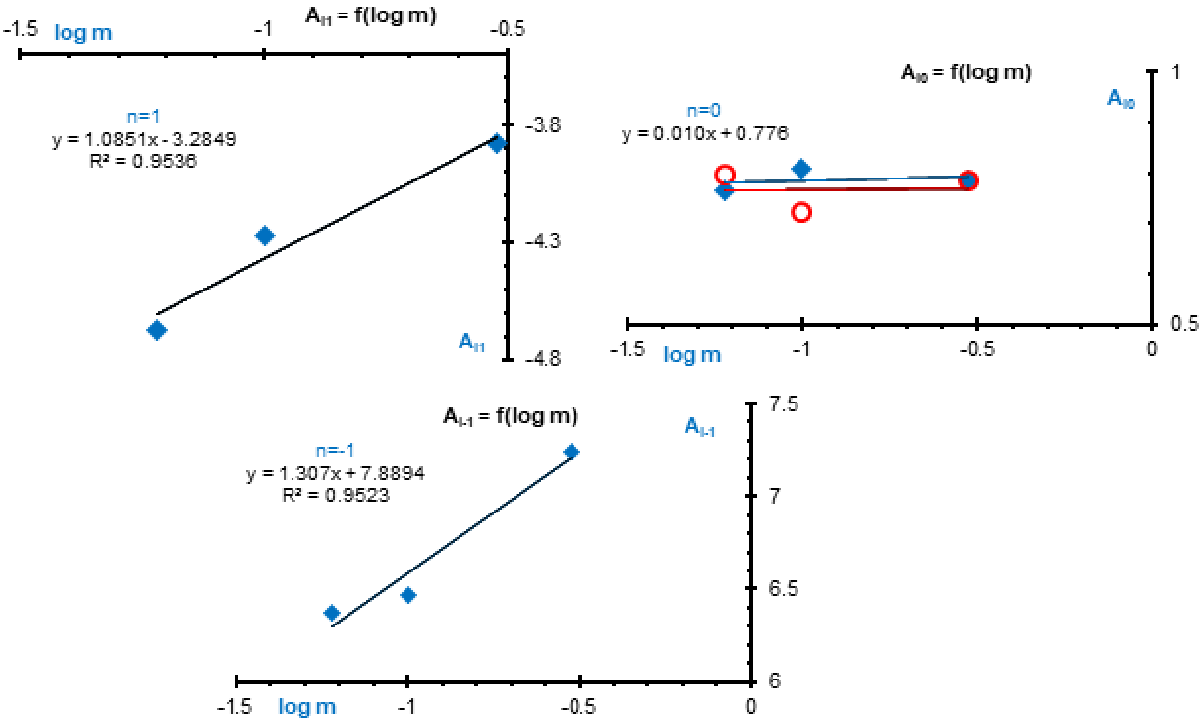

Fig 4. Variations of A_{ln} = f(log m) obtained for n = -1; 0 and 1 for different m

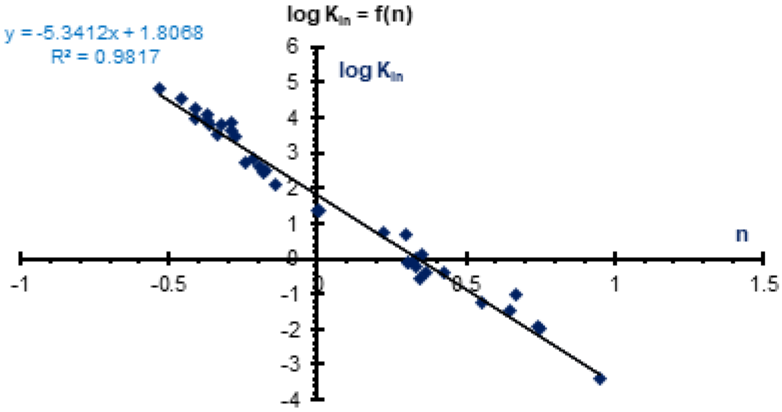

Fig 5. Variation log K_{1n} = f(n) obtained from m = 60, 100 and 300 mg/L

different surface protonation/deprotonation phenomena is shown in Fig. 5.

As found above, the straight line shows that the slope value equal to "n", varies between -1 and 1. Therefore, the constants K_{l0}, K_{l1} and K_{l-1} are the intersect and y-coordinates associated to (0,0); (1,1) and (1,-1) points of log K_{ln} = f(n), respectively. This information provides that the intrinsic constants K_{l0} or K_{00} (independent on l), is such log K_{00} = 1.81, log K_{11} = -3.53, and log K_{1-1} = 7.15. The apparent constant value related to n = 0.35 is such log $K_{10.35}$ = 0. Furthermore, the adsorption reaction associated with apparent constant $K_{l.z,1}$ is composed of mononuclear reaction (z%) and binuclear reaction ((1-z)%). This result can be used to calculate log $K_{2\pm1}$ according to:

$K_{1.1,1} = (K_{11})^{0.9}(K_{21})^{0.1}$

$K_{1.3,-1} = (K_{1-1})^{0.7}(K_{2-1})^{0.3}$

This allows for obtaining log K_{21} =-1.03 and log K_{2-1} = 9.62. Considering that adsorbed species are mono- and bidentate complexes, Table 1 summarizes the obtained results.

Table 1. Surface complexation and stability constants for Cr(VI) sorption onto Fe(III) hydroxide

(l,n)	Surface Complexation Reaction	log K_{ln}	pH
(0,0)	$\overline{> SOH_2^+} + H_{2-y}A^{(y-2)} \Leftrightarrow \overline{(> SOH_2^+)(H_{2-y}A)^{-y}}$ y = 1; 2	1.81 ± 0.04	pH ≤ 5.5
(1,1)	$\overline{> SOH_2^+} + H_{2-y}A^{(y-2)} \Leftrightarrow \overline{> SOH_2^+ - (H_{2-y}A)H_{-1}^{(y-3)}} + H^+$ y = 1; 2	-3.53 ± 0.07	pH ≤ 5.5
(2,1)	$2\overline{> SOH_2^+} + H_{2-y}A^{(y-2)} \Leftrightarrow \overline{> (SOH_2^+) - (H_{2-y}A)H_{-1} - S^{(y-3)}} + H_2O + H^+$ y=1; 2	-1.03±0.23	pH≤5.5
(1,-1)	$\overline{> SO^-} + A^{2-} + H_2O \Leftrightarrow \overline{> (SOH - A)^{2-}} + OH^-$	7.15 ± 0.14	pH ≥ 5.5
(2,-1)	$2\overline{> SO^-} + A^{2-} + H_2O \Leftrightarrow \overline{> (SOH - A - SO)^{4-}} + OH^-$	9.62 ± 0.53	pH ≥ 5.5

CONCLUSION

The adsorption of hexavalent chromium Cr(VI) on Fe(III) hydroxide was thoroughly investigated. For this purpose, a method was developed for studying the surface complexation of $Fe(OH)_3$ sorbent. The partition of Cr(VI) between the solid and liquid phases was examined as a sorbent mass function, contact time, and solution pH. The proton and hydroxyl ion exchange were evaluated to define the adsorption reaction and define surface complexes to achieve this purpose.

The study of log D = f(pH) experimental data (D = distribution coefficient = ratio of chromium in the solid and liquid phases), pointed out that the adsorption of Cr(VI) on Fe(III) hydroxide was greater than 90% in all cases, for pH values ranging between 4 and 6. Furthermore, the obtained results were used to specify the predominant chromium surface complexes. These results allowed the identification and formulation of these complexes according to the acidity of explored environments. These complexes concerned $\overline{> S(OH_2^+)(HA^-)}$; $\overline{> S(OH_2^+)(A^{2-})}$; $\overline{> S(OH_2^+)(H_1A^{-1})}$; $\overline{> S(OH_2^+)(A^{2-})}$; $\overline{> S(OH_1^0)(A^{2-})}$; $\overline{> (SOH_2^+) - (H_1A)H_{-1} - S^{(-2)}}$; $\overline{> (SOH_2^+) - AH_{-1} - S^{(-1)}}$; $\overline{> S(OH)(A^{2-})}$ and $\overline{> (SOH_2^+ - A - SOH)^{4-}}$. The complexing constants were calculated using the transformed curves of raw experimental data. The logarithmic values of these constants were: log K_{00} = 1.81 ± 0.04, log K_{11} = -3.53 ± 0.07, log K_{21} = -1.03 ± 0.23, log K_{1-1} = 7.15 ± 0.14 and log K_{2-1} = 9.62 ± 0.53. Therefore, Fe(III) hydroxide exhibited high adsorption capacity for hexavalent chromium. Therefore, this sorbent could be considered as excellent and reliable for the effective removal of Cr(VI) from wastewater solutions before dumping it into the environment.

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