ADSORPTION OF CITRIC ACID ON IRON (III) HYDROXIDE: MECHANISMS AND STABILITY CONSTANTS OF SURFACE COMPLEXES

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ABSTRACT
The adsorption of citrate ions H₃A (y=1, 2, 3 and A=H₃C₆O₇⁻³) on iron (III) hydroxide was conducted as a function of adsorbent mass, solution pH, and hydration time. The surface complexation technique, which is based on the examination of the distribution of the citrate ions between the solid and liquid phases, was adopted to predict the reaction mechanism, define the order, and calculate the values of stability constants of surface complexes. The experimental results obtained illustrate the sorption mechanisms involved, and the reactions associated with them, which are reactions by ion exchange of H⁺, OH⁻, and/or intrinsic reaction (zero exchange). The formulation of the surface complexes is made according to the acidity of the media explored, and the contact times. These species are: > S(OH)(HA⁻⁻) (C₁₀); > S(OH)(OH)(HA⁻⁻) (C₁₁, y=0); > S(OH)(OH)(HA⁻⁻) (C₁₁, y=1), > S(OH)(OH)(A⁻⁻) (C₁₁, y=2) and > S(OH)(A⁻⁻) (C₁, y=1), whose complexation constants are calculated using the curves transformed from raw experimental data. The logarithmic values of these constants are respectively logK₁₀ = 1.265; logK₁₁ = -5.345 and logK₁₂ = 7.87. Therefore, the iron (III) hydroxide Fe(OH)₃ could be considered an excellent sorbent for removing organic matter wastewater solutions.

Keywords: Adsorption, Surface Complexation, Citric Acid, Iron (III) hydroxide, Distribution coefficient “D”.

INTRODUCTION
Citric acid, H₃A (A=C₆H₈O₇⁻³) is an important organic acid, used on a large scale in the food and pharmaceutical industries¹,² and is produced, essentially, by a macro-fermentation process. The conventional recovery of this acid as calcium citrate is achieved by the precipitation method using hydrated lime. The obtained carboxylate salt is reconverted to the carboxylic form by sulphuric acid dissolution. Considerable amounts of low-value by-products such as gypsum (CaSO₄·2H₂O) are produced. To avoid this dilemma requires increasing the citric acid recovery and reducing waste regeneration by decreasing consumption of chemical products.³,⁴ A solvent extraction has been suggested as a prospective method of separation of citric acid from fermentation aqueous solution for the fermentation products. Citric acid (H₃A) enters water bodies through food products, cosmetics, pharmaceuticals, and industrial detergents.⁵-⁹ In excessive quantities, this acid impacts the quality of the drinking water. The discharge of this acid in the surface water is a serious threat to rivers, streams, and aquatic life. As a result, the public concerns raising in environmental pollution, require sustainable technologies for reducing organic water pollution.¹⁰,¹¹ To meet environmental regulation, wastewater discharge of citric acid industry was firstly treated by anaerobic-aerobic digestion. However, this digestion process and subsequent treatments cost a lot. Furthermore, large amounts of sulfate, calcium, and ammonia, as well as residual sludge, are subsequently produced and need further treatment. Accordingly, wastewater is still a managing difficulty for the C₆H₈O₇⁻³ industry.¹² The increasing requirement and use of citric acid require developing an efficient method with lower waste. Due to the low operation cost and minimal secondary pollution, adsorption is a required and attractive
technique, for this purpose. For water treatment, these techniques are usually performed using conventional or non-conventional adsorbents, especially, zeolites,16 and iron (III) hydroxide.17-21 However, adsorption is the technique of choice for the removal of dissolved elements, mostly organic,22,23 and trace metals.24-29 One can note that this procedure is often carried out using activated carbon.30,31 Nevertheless, iron oxyhydroxide or ferric oxyhydroxide (FeO(OH)) which is low soluble and often poorly crystalline has a large surface area and special surface active sites.32 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.33 The contribution of this exchange phenomenon to Q is dependent on the transfer of proton to hydroxo complex interface (>SOH) that is a function of the acidity of the suspension medium.34 As discussed previously, the proton transfer reaction can be treated as acid-base equilibrium after protonation/deprotonation of >SOH.34,36 Taking these considerations into account, the main objective of this study consists of co-precipitation or surface complexation of citrate ions on iron (III) hydroxide. For this purpose, the sorption of C₆H₈O₇ is examined through co-precipitation experiments, from an aqueous solution, as a function of adsorbent mass, contact time, and equilibrium pH of citrate solution 2.75x10⁻³ M. The ion exchange method, previously used with success in liquid-liquid extraction, was carried out, to examine the sorption and the complexation of citrate anion with the surface of amorphous Fe(OH)₃, xH₂O.

EXPERIMENTAL

Materials and Methods
Chemicals namely citric acid (C₆H₈O₇, H₂O)(99%), Sodium hydroxide (NaOH)(99%), Potassium permanganate (KMnO₄)(99%), iron (III) chloride (FeCl₃) (99%), and Nitric acid (HNO₃) (99%), were used and purchased from Sigma Aldrich. The reagents are of analytical grade and used without further purification.37 High-quality distilled water is used for all of the experiments.

Instrumentation
The equipment used in this research was a laboratory balance ADB, KERN of precision 10⁻⁴ g, MIKRO 200 HETTICH benchtop centrifuge, and magnetic stirrer. The measurement of pH of sample solutions was carried out by using METROHM pH-meter of precision 10⁻³ pH unit, equipped with a double concentric electrode previously calibrated. The dosage of citric acid is carried out in the aqueous phases by the permanganate index technique.

Procedure
The adsorption studies were carried out by co-precipitation of Fe(OH)₃. The iron (III) masses used in this case are equal to 0.2, 0.3, 0.5, and 1.0 g/L, while the contact time is varied in the range 0.5 h-24 h. The concentration of citric acid in the examined media is equal to 2.7x10⁻³ M, these suspension media are obtained from stock solution molarity 5.4x10⁻² M. The pH of the solutions is attuned by equimolar solutions of NaOH or HNO₃.

Adsorption Experiments
The dosage of citric acid in the aqueous solution is carried out by the volumetric technique called permanganate index. This technique consists of a direct determination of this acid by potassium permanganate in an acid medium according to the following oxidation-reduction reaction:

\[
18\text{MnO}_4^- + 5\text{C}_6\text{H}_8\text{O}_7^- + 54\text{H}^+ \rightarrow 18\text{Mn}^{2+} + 30\text{CO}_2 + 47\text{H}_2\text{O}
\] (1)
For this purpose, a sample of V1=20ml of the liquid phase acidified with 1ml of 2x10^{-3}M sulfuric acid is assayed directly with the permanganate solution C(KMnO4)=2.7x10^{-3} M. The equivalence point is marked by the color change to purple.

The co-precipitation of citric acid by Fe(OH)₃ is examined as a function of pH, which varied between 3 and 12. The results obtained are plotted as curves logD=f(pH).

The distribution of organic matter between the two phases is characterized by the partition coefficient “D” defined by the ratio of equilibrium concentrations of citric acid between the solid and liquid phases.

\[
D = \frac{[C₆H₈O₇]_{solid}}{[C₆H₈O₇]_{liquid}}
\]

With [C₆H₈O₇] the concentration of solid-phase citric acid (adsorbed), and [C₆H₈O₇] the concentration of citric acid in the aqueous phase (not adsorbed).

“D” can be obtained from the elimination percentage P, by the relation:

\[
D = \frac{P}{1-P}
\]

Mechanism of Adsorption and Surface Complexation

In general, the process of adsorption of weak acids (organic and inorganic) with hydrated oxides is described by a complexation reaction of acids with active sites > S – OH. The acid-base properties of the surface of the adsorbents considered are attributed to the protonation/deprotonation reactions which take place on the surface of the sorbent and which can be expressed by:

\[
(>S – OH) + H^+ \leftrightarrow (>S – O) + H^+ \quad K^+
\]

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

The symbols H₁ and Hᵢ respectively denote the H atoms and the OH group. This leads therefore to:

\[
H_{-1} + H_{1} \leftrightarrow H_{2} O
\]

The adsorption of organic acids H₃A by Iron hydroxide can be described by the Sillen notation, generally adopted in complexing reactions in the aqueous phase.

\[
\text{i} \quad \text{SOH} + H_{3-y}A^y \leftrightarrow (>\text{SOH})H_{(3-y-n)}A + n\text{H}^+; \quad K_{ln}
\]

With: \( y=0; 1; 2; 3 \) and \( A=C₆H₈O₇^+= \)ion citrate

Taking into account the expression of “D” given by:

\[
D = \frac{|(>\text{SOH})H_{(3-y)}A|}{|H_{y}A^+(\text{aq})|}
\]

The surface complexation constants for equilibrium is:

\[
K_{ln} = \frac{|(>\text{SOH})H_{(3-y)}A|}{|H_{y}A^+(\text{aq})|} \quad |H_{y}A^+(\text{aq})| \quad \text{m}^{-1} \quad \text{m}^{-1}
\]

So that:

\[
\log D = \log K_{ln} + m \log m + n \text{pH}
\]

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According to expressions mentioned below, the study of the variation in the value of the distribution coefficient “D” as a function of pH, allows to verify the supposed binding mechanism involved “l”, determine the nature ‘n’ of the adsorbed species, and calculate the $K_l$ constants.

\[
\frac{\partial D_0}{\partial pH} = n
\]  
\[
\frac{\partial \log D}{\partial \log m} = l
\] 

(11)  
(12)

**RESULTS AND DISCUSSION**

Effect of pH

The experimental results of the adsorption of citrate ions on iron hydroxide are given in Fig.-1, as a logarithmic variation of “D” with pH for iron (III) contents equal to 0.2, 0.3, 0.5, and 1.0 g/L at contact times ($t_c$) of 0.5, 1, 4, and 24 h. One can note that these curves are to define the mechanisms of citric acid adsorption involved in this case.

These results show that the logD variations with the pH are described by a parabolic equation with a correlation coefficient ($R^2$) $\geq 85\%$. Therefore, logD increases with the pH until reaching a maximum in the pH range between 4.5 and 8.5, and above pH 8.5 logD decreases almost linear. This variation is particularly related to the phenomenon of protonation/deprotonation of active sites \( S = O H \) of the sorbent surface combined with those of the adsorbate.\(^{38-40}\) This variation is generally characteristic of the adsorption of weak acids, whose adsorption is maximal in the vicinity of their $pK_a$.

In this case, the $pK_{a1}$ values are equal to $pK_{a1} = 3.13$, $pK_{a2} = 4.76$ and $pK_{a3} = 6.4$. When the pH becomes greater than $pK_{a3}=6.4$, the citric acid is...
mainly in anionic form, which leads to a repulsion with the surface of the sorbate when it is negative. It is noted that the zero charge point (PZC) of the iron hydroxide is of the order of 7. Thus the surface of this hydroxide is positively charged in the case pH<PZC, and negatively for pH>PZC. These results show a maximum in the field of 4.5 < pH < 8.5. Two overlaps are observed at pH equal to 5.2 and 9.8. It appears that the first overlap occurs at pH= pK_a active sites > S − OH iron (III) hydroxide whose pK_a is close to 5.4. The second overlap occurs when the load or the potential of the surface of the sorbent material is reduced.

Effect of Absorbent Mass

Figure- 2 shows the variations logD=f(pH) which correspond to m= 0.2, 0.3, 0.5, and 1.0 g/L and a contact time t_ct = 1 h.

We observe a negligible effect of the sorbent content for m>0.2g in the acidic field. However, in the basic domain, this effect becomes more significant. However, there is no simple relation of this effect with m. Fig.-3, shows the results obtained for t=4h.

In this case, there is also a negligible effect of the mass of iron (III) hydroxide in the acidic zone. However, this effect becomes significant for pH values greater than about 6.5. Indeed the adsorption is all the more important as m is high.

Variation of logD=f(logm)

From the previous results, we have deduced logD=f(logm) at pH constant. Figure-4 and 5, show the results obtained in this case.
Figure-4 and 5, show, that the variations $\log D = f(\log m)$ are perfectly described by a cubic polynomial equation ($R^2 = 1$), in all cases. A maximum is always obtained for $\log m = -0.3$ ($m = 0.5\, g$). However, to define the average stoichiometric coefficient of the sites $> S - OH$ which are involved in the adsorption reaction, we have determined the slopes of the straight lines $\log D = f(\text{pH})$ obtained in the domain $-0.7 < \log m < -0.3$. The slope values are of the order of $l = 1$ for pH $< 6$ and $l = 0$ for pH $= 6$. As a result, the adsorption process is a mononuclear ($l = 1$) uptake Mechanism. Besides, the slope value equal to zero obtained at pH $= 6$ indicates that under optimal conditions the complexation reaction is almost complete and is therefore independent of $m$.\textsuperscript{46,47}

**Variation of $\frac{\partial \log D}{\partial \text{pH}} = f(\text{pH})$**

As shown above in Eq. (11), $\frac{\partial \log D}{\partial \text{pH}} = n$, corresponds to proton $H^+$ ($n > 0$) or hydroxyl OH$^-$ ($n < 0$), exchanged during the surface complexation reaction described by Eq. (7). Obtained results show that the mechanism of citric acid adsorption with Fe(OH)$_3$ sorbent occurs via electrostatic attraction or diffusion process ($\frac{\partial \log D}{\partial \text{pH}} = 0$), proton ($\frac{\partial \log D}{\partial \text{pH}} > 0$) and hydroxyl ($\frac{\partial \log D}{\partial \text{pH}} < 0$) exchanges.

To determine the ‘$n$’ values and to deduce therefore the adsorption mechanism of citrate ions involved in this case, the experimental data, $\log D = f(\text{pH})$ are fitted with cubic polynomial equation ($R^2 > 0.98$), in various pH regions.\textsuperscript{48,49}
Figure-6 shows the variations n=f(pH) obtained for m=0.2, 0.3, 0.5, and 1.0 g/L of iron (III), and contact times varying between 0.5 h and 24 h.

In all cases, the variations n=f(pH) exhibits a similar behavior that is varying significantly with the contact time, in acid conditions. The protonation/deprotonation phenomena of the sorbent depend on the surface coverage and vary between -1 and 1 for m=0.2, 0.3, 0.5, and 1.0 g/L. So that, the species associated with intrinsic adsorption (n=0) predominate in the pH range between 5 and 8. However, the surface complexes due to proton exchange (n=+1) are generally predominant in very acidic environments (pH<4). As for the species which corresponds to n=-1, this predominates in basic environments. It follows from this mechanism the surface complexes (C_{n}), whose nature depends on the acidity of the aqueous medium. These species are C_{10}, C_{11}, and C_{1-1}.

Figure-6: n Versus pH for Various Contact Times, and Different Sorbent Amounts

Citric Acid Adsorption Mechanism and Stability Constants

Variation of logK_{ln} = f (n)

The complexation equilibrium constants (K_{ln}) are obtained from the line segments of the logD=f(pH) curves obtained for the different contents of "m" which varied between 0.2 and 1.0 g/L. The slope of these segments leads to the value of ‘n’. The y-intercept of these lines which is equal to A_{ln}=logK_{ln} + logm leads to the value of logK_{ln}, which is equal to A_{ln}-logm.

The values of ‘n’, the values of A_{ln}, and the values of logK_{ln} allow the calculation of the constants of formation of the identified complexes. The refinement of these segments (y) is described by first-order equations, whose correlation coefficient, R^2 is often greater than 85%. Fig.-7, illustrates the logK_{ln} variations as a function of ‘n’.

As found above in Fig.-7, the variations K_{ln} = f (n) are described by a linear equation (R^2 = 0.98) in the entire field of ‘n’ explored. The values of the intrinsic constants, K_{ln}, which correspond to physical
adsorption (species C_{10}), adsorption by exchange of H^+ (C_{11}), and adsorption by exchange of OH^-(C_{-1}) are defined from the equation of the straight line whose expression is logK_{ln} = -6.611.n + 1.265. The definition of surface complexes requires knowledge of the distribution diagram of citric species as a function of pH. We note that the values of the pKa of this acid are respectively equal to pka1 = 3.132, pka2 = 4.76, and pka3 = 6.4.

The logarithmic values of the complexation constants are obtained from the equation logK_{ln} = -6.611.n + 1.265, are given in Table-1.

![Graph](image)

**Fig.-7:** Variations logK_{ln}=f(n) obtained for m=0.2, 0.3, 0.5, and 1.0 g/L

The logarithmic values of the complexation constants are obtained from the equation logK_{ln} = -6.611.n + 1.265, are given in Table-1.

| (l,n) | Surface Complexation | logK_{ln} | pH     |
|------|----------------------|-----------|--------|
| (1,0) | > SOH_{2}^{+}+HA^{-} ↔ > SOH_{2}^{+}−H_{2}A(−2) | 1.265     | 5<pH<8 |
| (1,1) | > SOH_{2}^{+}+H_{3,y}A^{(y)} ↔ > SOH_{2}^{+}−(H_{3−y}A)H_{2−y}(−3−y) + H^{+} y = 0,1 or 2 | -5.345 | pH<6   |
| (1,-1) | > SO^{−}+A^{3−}+H_{2}O ↔ > S(OH)(A^{3−}) + OH^{−} | 7.87     | pH>7.5 |

**CONCLUSION**

The adsorption of citric acid on iron (III) hydroxide was thoroughly investigated. For this purpose, a method was developed for studying the surface complexation of citric acid with this sorbent. The partition of this acid between the solid and liquid phases was examined as a function of the sorbent mass, contact time, and solution pH. The proton and hydroxyl ion exchange was evaluated to define adsorption reaction and define surface complexes to achieve this purpose.

The treatment of logD=(pH) experimental data (D=distribution coefficient), pointed out that the adsorption of citric acid on iron (III) hydroxide was greater than 90% in all cases, for pH values ranging between 6 and 7. Furthermore, the obtained results were used to specify the predominant citrate surface complexes and allow the identification and formulation of surface complexes according to the acidity of the environments explored. These species are > S(OH_{2}^{+})(H_{2}A^{−2}) (C_{10}), > S(OH_{2}^{+})(H_{2}A^{−3}) (C_{11}, y=0); > S(OH_{2}^{+})(H_{2}A^{−2}) (C_{11}, y=1), > S(OH_{2}^{+})(A^{−3}) (C_{11}, y=2) and > S(OH)(A^{−3}) (C_{11}). The complexing constants are calculated using the transformed curves of raw experimental data. The logarithmic values of these constants are logK_{C_{10}} = 1.265; logK_{C_{11}} = -5.345 and logK_{C_{11}} = 7.87.

Taking into account these considerations, iron (III) hydroxide exhibits a high adsorption capacity for organic acid. Therefore, this sorbent could be considered excellent and reliable for the effective removal of citric acid from wastewater solutions before dumping it into the environment.
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