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 $H_{3-y}A$ ($y=1, 2, 3$ and $A=H_3C_8O_7^{3-}$) 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: $>S(OH_2^+)(HA^{2-})$ (C_{10}), $>S(OH_2^+)(H_2A^{-1})$ ($C_{11}, y=0$); $>S(OH_2^+)(HA^{2-})$ ($C_{11}, y=1$), $>S(OH_2^+)(A^{3-})$ ($C_{11}, y=2$) and $>S(OH)(A^{3-})$ (C_{1-1}), whose complexation constants are calculated using the curves transformed from raw experimental data. The logarithmic values of these constants are respectively $\log K_{10} = 1.265$; $\log K_{11} = -5.345$ and $\log K_{1-1} = 7.87$. 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”.

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INTRODUCTION

Citric acid, H_3A ($A=C_3H_8O_7^{3-}$) is an important organic acid, used on a large scale in the food and pharmaceutical industries^{1,2} 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 ($CaSO_4 \cdot H_2O$) 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 (H_3A) 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.¹⁰⁻¹⁴ 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 $C_6H_8O_7$ industry.¹⁵

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, zeolites¹⁶, 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.²⁴ 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.

The relevance of co-precipitation is deduced using the ratio of citric acid in solid and aqueous phases, which corresponds to the distribution coefficient "D". The concentration of citric acid is measured by the permanganate index technique.

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:

For this purpose, a sample of $V_1=20\text{ml}$ of the liquid phase acidified with 1ml of $2 \times 10^{-2}\text{M}$ sulfuric acid is assayed directly with the permanganate solution $C(\text{KMnO}_4)=2.7 \times 10^{-3}\text{M}$. The equivalence point is marked by the color change to purple.

The co-precipitation of citric acid by $\text{Fe}(\text{OH})_3$ is examined as a function of pH, which varied between 3 and 12. The results obtained are plotted as curves $\log D=f(\text{pH})$.

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.

$$D = \frac{[\overline{\text{C}_6\text{H}_8\text{O}_7}]}{[\text{C}_6\text{H}_8\text{O}_7]} \quad (2)$$

With $[\overline{\text{C}_6\text{H}_8\text{O}_7}]$ the concentration of solid-phase citric acid (adsorbed), and $[\text{C}_6\text{H}_8\text{O}_7]$ the concentration of citric acid in the aqueous phase (not adsorbed).

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

$$D = \frac{P}{1-P} \quad (3)$$

$$\text{With } P = \frac{|\overline{\text{C}_6\text{H}_8\text{O}_7}|}{|\text{C}_6\text{H}_8\text{O}_7|_{\text{total}}}$$

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 $\overline{\text{S}-\text{OH}}$. 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:

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:

The adsorption of organic acids H_3A by Iron hydroxide can be described by the Sillen notation, generally adopted in complexing reactions in the aqueous phase.

With: $y=0; 1; 2; 3$ and $\text{A}=\text{C}_3\text{H}_8\text{O}_7^{3-}$ =ion citrate

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

$$D = \frac{[(\overline{\text{SOH}})\text{H}_{3-y-n}\text{A}^{(3-y-n)}]}{|\text{H}_{3-y}\text{A}^{(y)}|} \quad (8)$$

The surface complexation constants for equilibrium is:

$$\text{K}_{\text{ln}} = \frac{[(\overline{\text{SOH}})_l \text{H}_{(3-y-n)}\text{A}^{(3-y-n)}] |\text{H}^+|^n}{|\text{H}_{3-y}\text{A}^{(y)}| |\overline{\text{SOH}}|^l} \quad (9)$$

$$\text{K}_{\text{ln}} = \frac{[(\overline{\text{SOH}})_l \text{H}_{(3-y-n)}\text{A}^{(3-y-n)}] |\text{H}^+|^n}{|\text{H}_{3-y}\text{A}^{(y)}| m^l} = D \cdot |\text{H}^+|^n / m^l \quad \text{where: } m = |\overline{\text{S}-\text{OH}}|$$

So that:

$$\log D = \log K_{\text{ln}} + l \log m + n \text{pH} \quad (10)$$

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_{ln} constants.

$$\frac{\partial \log D}{\partial \text{pH}} = n \quad (11)$$

$$\frac{\partial \log D}{\partial \log m} = 1 \quad (12)$$

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_{ct}) 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.

Fig.-1: logD Versus pH for Different Contact Times and Different Amounts of Iron (III)

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 $\overline{S-OH}$ 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_{ai} . In this case, the pK_{ai} 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 $\text{pH} < \text{PZC}$, and negatively for $\text{pH} > \text{PZC}$.^{41,42} These results show a maximum in the field of $4.5 < \text{pH} < 8.5$. Two overlaps are observed at pH equal to 5.2 and 9.8. It appears that the first overlap occurs at $\text{pH} = \text{pK}_a$ active sites $\text{>S}-\text{OH}$ 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.⁴³

Effect of Absorbent Mass

Figure- 2 shows the variations $\log D = f(\text{pH})$ which correspond to $m = 0.2, 0.3, 0.5$, and 1.0 g/L and a contact time $t_{\text{ct}} = 1 \text{ h}$.

Fig.-2: $\log D$ Versus pH for Contact Time $t_{\text{ct}} = 1 \text{ h}$ and Different Amounts of Iron (III)

We observe a negligible effect of the sorbent content for $m > 0.2 \text{ g}$ 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 $t = 4 \text{ h}$.

Fig.-3: $\log D$ Versus pH for Contact Time $t_{\text{ct}} = 4 \text{ h}$ and Different Amounts of Iron (III)

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.^{44,45}

Variation of $\log D = f(\log m)$

From the previous results, we have deduced $\log D = f(\log m)$ 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 $\log m = -0.3$ ($m = 0.5\text{g}$). However, to define the average stoichiometric coefficient of the sites $\overline{S - OH}$ 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 $\text{pH} < 6$ and $l=0$ for $\text{pH} = 6$. As a result, the adsorption process is a mononuclear ($l=1$) uptake Mechanism. Besides, the slope value equal to zero obtained at $\text{pH} = 6$ indicates that under optimal conditions the complexation reaction is almost complete and is therefore independent of m .^{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 $\text{Fe}(\text{OH})_3$ 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.^{48,49}

Fig.-4: $\log D$ Versus $\log m$ for Contact Time $t_{ct} = 1$ h and $\text{pH} = 3, 4, 6, 9$.

Fig.-5: $\log D$ Versus $\log m$ for Contact Time $t_{ct} = 4$ h, and $\text{pH} = 3, 4, 6, 9$.

Figure-6 shows the variations $n=f(\text{pH})$ 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 $n=f(\text{pH})$ 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 ($\text{pH}<4$). As for the species which corresponds to $n=-1$, this predominates in basic environments. It follows from this mechanism the surface complexes (C_{ln}), whose nature depends on the acidity of the aqueous medium. These species are C_{10} , C_{11} , and C_{1-1} .

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

Citric Acid Adsorption Mechanism and Stability Constants

Variation of $\log K_{ln} = f(n)$

The complexation equilibrium constants (K_{ln}) are obtained from the line segments of the $\log D=f(\text{pH})$ 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 $A_{ln}=\log K_{ln} + \log m$ leads to the value of $\log K_{ln}$, which is equal to $A_{ln}-\log m$.

The values of ' n ', the values of A_{ln} , and the values of $\log K_{ln}$ 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 $\log K_{ln}$ 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_{1-1}) are defined from the equation of the straight line whose expression is $\log K_{ln} = -6.611.n + 1.265$.

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 $pka3 = 6.4$.

Fig.-7: Variations $\log K_{ln}=f(n)$ 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 $\log K_{ln} = -6.611.n + 1.265$, are given in Table-1.

Table-1: Values of the Surface Complexation Constants of Citric Acid (H_3A) with Iron (III) Hydroxide

(l,n)	Surface Complexations	$\log K_{ln}$	pH
(1,0)	$\overline{>SOH_2^+} + HA^{-2} \rightleftharpoons \overline{>SOH_2^+ - H_1A^{(-2)}}$	1.265	$5 < pH < 8$
(1,1)	$\overline{>SOH_2^+} + H_{3-y}A^{(-y)} \rightleftharpoons \overline{>SOH_2^+ - (H_{3-y}A)^{H_{-1}^{(-1-y)}}} + H^+$ $y = 0,1 \text{ or } 2$	-5.345	$pH < 6$
(1,-1)	$\overline{>SO^-} + A^{3-} + H_2O \rightleftharpoons \overline{>S(OH)(A^{3-})} + OH^-$	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 $\log D=(pH)$ 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 $\overline{>S(OH_2^+)(HA^{2-})}$ (C_{10}), $\overline{>S(OH_2^+)(H_2A^{-1})}$ (C_{11} , $y=0$); $\overline{>S(OH_2^+)(HA^{2-})}$ (C_{11} , $y=1$), $\overline{>S(OH_2^+)(A^{3-})}$ (C_{11} , $y=2$) and $\overline{>S(OH)(A^{3-})}$ (C_{1-1}). The complexing constants are calculated using the transformed curves of raw experimental data. The logarithmic values of these constants are $\log K_{10} = 1.265$; $\log K_{11} = -5.345$ and $\log K_{1-1} = 7.87$.

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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