



Determination of Surface Parameters of Iron(III) Hydroxide Sorbent

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The surface layer parameters of iron(III) hydroxide were studied. The surface charge, the sorption of proton H^+ , hydroxyl OH^- as a function of hydration time (T_{CT}), the pH of the suspension solution and the sorbent concentration were presented. For this purpose, two methods were chosen: potentiometric mass titration (PMT) and potentiometric time titration (PTT). The concentrations suspensions used were 20, 40 and 60 g/L. The variations of surface charge with the time contact, $Q = f(T_{CT})$ were examined for hydration time ranging from zero to 72 h. The isoelectric point (IEP) and point zero charge (PZC) were defined using the variations $pH = f(T_{CT})$ resulting from protonation/deprotonating of surface sites $>S-OH$ with derivative methods $d(pH)/d(T_{CT}) = f(pH)$ the values of PZC and IEP were found: $PZC = 7.45 \pm 0.1$ and $IEP = 7.65 \pm 0.1$.

Keywords: Iron hydroxide, Potentiometric, Adsorbent, Surface charge, Point zero charge, Isoelectric point.

INTRODUCTION

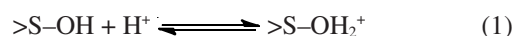
Organic contaminants, mostly discharged from hospitals [1-3], industrial processes [4-7], human waste [8,9] and inorganic contaminants such cobalt, zinc and copper, are the most common types of contaminants found in water. However, other elements, such as cadmium, arsenic, chromium, mercury and lead are toxic and undesirable [10,11]. The quantity of suspended solids particles, quality of water and the amount of transition and heavy metals in these effluents must be minimized in order to address environmental concerns [12-14].

For this purpose, several methods, such as solvent extraction [15,16], ion exchange [17], precipitation [18], liquid-liquid extraction and adsorption [19,20] are used. Among these techniques, adsorption takes a prominent place as process to minimize the concentration of trace metals from diverse pollution sources [21-24]. This approach is applied to numerous adsorbents, including coal, zeolites, silica and iron hydroxide [25]. Iron hydroxide is known for its high adsorption ability for trace metals and has a specific surface area of order $100 \text{ m}^2/\text{g}$ [26,27].

The surfaces of mineral particles are most often charged in an aqueous solution. Several effects can be at the origin of

surface charge [28-31]. The initial principle, applicable regardless of the mineral's characteristics, which arises from the disparity between the atomic environment of surface particles as well as of the core particles. The coordination number of the surface atoms is consequently decreased in comparison to that of the same atom within the crystal lattice due to the absence of bonds. To overcome this unfavourable energy state, the surface surroundings undergo the adsorption of water molecules. These adsorbed molecules can dissociate and form surface groups of the type $>S-OH$. These groups can easily capture or release protons depending on the pH of the medium to form charged surface species such as $>S-OH_2^+$, $>S-O^-$, $>OH_2^+$ and $>O^{2-}$.

The fact that the particles were charged induces the formation of a double electrical layer around them. This zone corresponds to the solid/solution interface where ions and co-ions compensate for the surface charge. The ions and co-ions are point charges, which are organized to form a "diffuse-double layer". In conventional models, all the reactions are considered as an equilibrium. Moreover, the surface proteolysis, where H^+ transfers among chemicals, is represented as follows:





where the $>S-OH$ represents a species or functional groups on a solid surface. In first reaction, $>S-OH$ gains an H^+ and becomes positively charged, while in second reaction, $>S-OH$ loses an H^+ and becomes negatively charged. Consequently, the surface charge of adsorbents exhibits a significant dependence on the pH of the aqueous medium. When the total sum of the surface positive and negative site charges is zero, the pH value of the aqueous solution corresponds to the point of zero charge (PZC). However, in presence of the specific adsorption or surface impurity, then the pH value corresponding to zero total surface charge corresponds to the isoelectric point (IEP) of adsorbent [9]. This theory of choice describes the dependence of surface charges on the pH of aqueous solution. Indeed, when the pH of solution is higher than the PZC, then the surface of solid acquires a negative charge and becomes more capable of exchanging cations, while the solid surface retains anions if the pH of aqueous solution is higher than its PZC. The PZC determines the capacity with which an adsorbent can adsorb harmful pollutants [10].

Enhancing the application of iron(III) hydroxide in water treatment to manage its surface interactions with both organic and inorganic pollutants requires a thorough investigation of this adsorbent's surface characteristics. Thus, in this work, the values of its surface physico-chemical parameters, specifically the point of zero charge (PZC) and the isoelectric point (IEP) were evaluated [32].

EXPERIMENTAL

Analytical grade chemicals procured from Sigma-Aldrich, USA for this study were sodium hydroxide (99%), nitric acid (99%), sodium chloride (99%), hydrochloric acid (37%), sodium chloride (99%), iron(III) chloride and sodium nitrate (99%) and used without further purification. High-quality distilled water was used for all the experiments.

The equipment used in this study was a laboratory balance ADB, KERN of precision 10^{-4} g, MIKRO 200 HETTICH bench-top centrifuge and magnetic stirrer. The measurement of the pH of sample solutions was carried out by using a METROHM pH-meter of precision 10^{-3} pH unit, equipped with a double concentric electrode previously calibrated.

General procedure: The colloidal solutions of iron(III) hydroxide used for surface chemistry characterization were set by quick addition of NaOH (0.05 M) to acid solutions of iron(III). The solutions used correspond to 20, 40 and 60 g iron(III) chloride per litre of solutions. The surface chemistry was undertaken for different parts. Experiments are conducted to investigate the effect of the initial sorbent dose on surface protonation/deprotonation.

Ionization experiments of surface sorbent were examined using the technique of protonation/deprotonating of sorbent material. This technique was carried out in the batch adsorption technique. The extent of H^+/OH^- exchange with $Fe(OH)_3$ was achieved by examining the effect of experimental variables such as pH, adsorbent dose 20, 40 and 60 g/L and contact time. The obtained results were applied to determine the point of

zero charge (PZC), isoelectric point (IEP) and surface charge (Q). To achieve this purpose, titrations of HNO_3 (0.05 M) sorbent systems were carried out at room temperature with $NaNO_3$ (0.05 M). Surface charge variations against time (T_{CT}) were examined for various mass solutions (20, 40 and 60 g/L).

Adsorption studies: The conventional potentiometric technique was used to determine the values of the zero charge point (PZC), isoelectric point (IEP) and surface charge (Q). The pH of colloidal solutions can be monitored as a function of hydration time and V (NaOH). The solutions used were obtained by dissolving different quantities of iron(III) chloride ($m = 0.5, 1$ and 1.5 g), *i.e.* (20, 40 and 60 g/L) in 25 mL of NaOH (0.05 M). The hydration times ranged from 15 min to 72 h for all initial pH (pHi: range from 3 to 11). The initial pH was adjusted by adding HCl (0.05 M) or NaOH (0.05 M). The acidity constants of the sorbent used were obtained by modeling the potentiometric titration curves of this material.

RESULTS AND DISCUSSION

Effect of pH: The acid-base properties of an ionic species are strongly defined by the surface charge (Q) of that species. For solid solutions, this load changes nature (sign) at the point PZC. This point represents, in the context of zeta-metric measurements, the location where the sign of ζ changes, which is also referred to as Z. Regarding the potentiometric measurements, this point of zero charge is none other than the inflection point of the $pH = f(T_{CT})$ variations. This PZC parameter can therefore be obtained from the derivative of the function $pH = f(T_{CT})$ which is, therefore, smoothed by the polynomial equations. The surface charge Q of a solid solution therefore varies depending on the pH of the solution medium. The electrostatic nature (positive or negative charge) of this charge also changes with the contact time (T_{CT}). Indeed, from the point PZC, a conversion of the sign of Q was also observed. The point PZC is, therefore, an inflection point that can be obtained from the variations $dpH/dt = f(pH)$.

The $dpH/dt = f(pH)$ variations correspond to the different colloidal solutions examined are presented in Fig. 1. The adsorbent mass "m" is an important factor that governs the protonation/deprotonating process performance. This factor was studied to give more precise PZC and IEP values.

In all cases, Fig. 1, shows the variation of the H^+ , OH^- adsorption/desorption rate $dpH/(dT_{CT}) = f(pH)$ for $m = 20, 40$ and 60 g/L. The hydration time ranged from 15 min to 72 h for different initial pH. However, in a basic medium, at pH higher than 7.2, the sorbent hydration was governed by the deprotonating of surface sites $>S-OH$ to give $>S-O^-$.

The isoelectric point is defined as being the pH value, where the net surface charge is zero and does not depend on hydration time. It corresponds to the point of intersection of $dpH/(dT_{CT}) = f(pH)$ curves with each other. The PZC point is identified as the point of intersection of the $dpH/(dT_{CT}) = f(pH)$ curves with the x-axis, while the IEP point corresponds to the point of intersection of these curves with each other. In general, the PZC value depends on the adsorption of electrolyte ions (Na^+ , Cl^-). Hence, the adsorption of electrolyte anion on a negatively (positively) charged surface increase (decrease) in the isoelec-

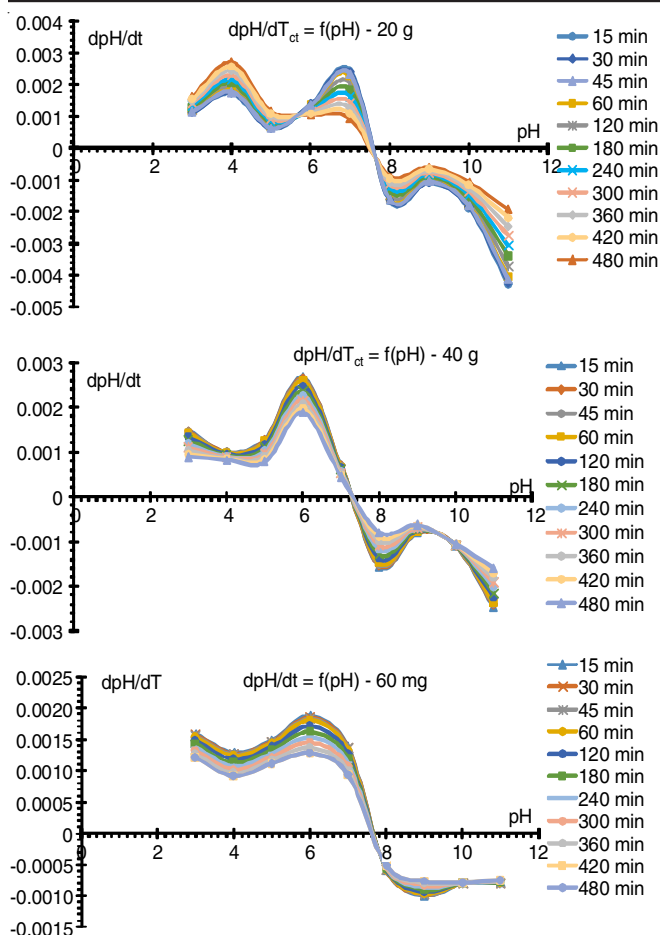


Fig. 1. Variation in $(dpH/dt)_{T_{ct}} = f(pH)$ obtained for a substrate suspension of $m = 20, 40$ and 60 g/L

tric point and a decrease (increase) in the point of zero charge, however, adsorption of cation showed the reverse effect.

The results show that the values for PZC and IEP were found to be $PZC = 7.45 \pm 0.1$ and $IEP = 7.65 \pm 0.1$, respectively. The small difference between IEP and PZC is due particularly to chloride or sodium ions adsorption. These values are in agreement with the reported data [33].

Potentiometric time titration (PTT): The titration of the $Fe(OH)_2(m)$ -HCl (0.05 N) solution was carried out with NaOH (0.05 M), respectively for $m = 20, 40$ and 60 g/L. The suspension time of hydration of this sorbent varies between 16 and 72 h. The plots of the surface deprotonating/dehydroxylation as a function of pH in the absence of electrolytes as depicted in Fig. 2. For $m = 20$ g/L, it appears that for all contact times, the sorbent considered has a basic character. However, when the hydration time becomes more and more important, the sorbent shows a less and less basic character, this character is associated with the formation of a positive charge.

For $m = 40$ g/L, the obtained variations show a neutralization of the acidic medium. This neutralization is all the more important as the hydration time of the solution is high, which has the opposite effect to that observed for 20 g/L solution. For $m = 60$ g/L, the variations obtained show a neutralization of the acidic medium that is not dependent on the hydration time.

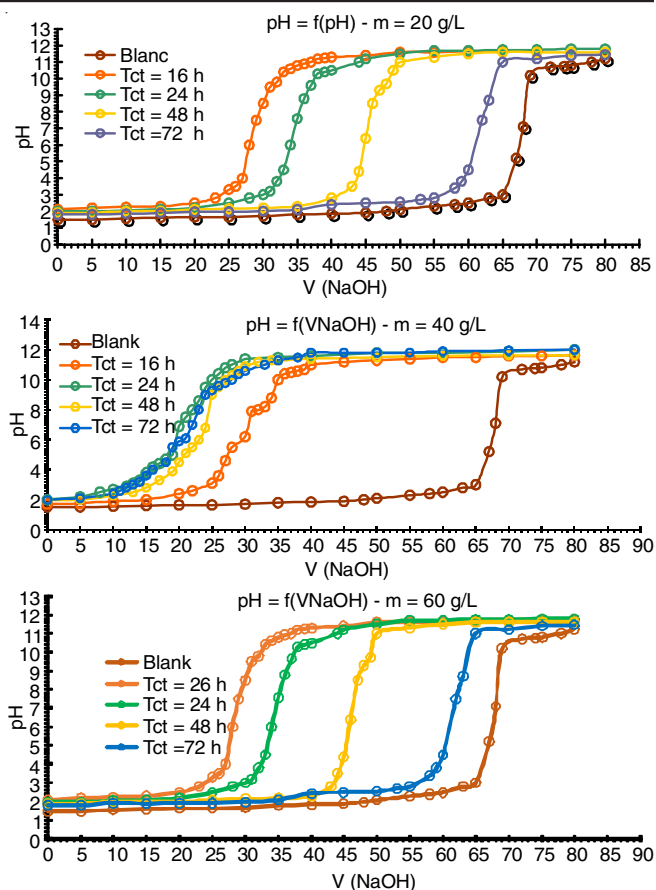


Fig. 2. Variations in $pH = f(VNaOH)$ obtained for a substrate suspension $m = 20, 40$ and 60 g/L at different hydration times

Surface charge of $Fe(OH)_3$: A complementary method is used to evaluate the point of zero charge, which involves the variation in the surface charge Q as a function of pH. This method is based on the evaluation of the quantity of H^+ proton or OH^- hydroxyl groups adsorbed on the surface. This is achieved according to:

$$Q = \frac{F \times C \times \Delta V}{m}$$

where F is the Faraday constant; C is the concentration of titrating acid/base; ΔV is the difference in the volume of acid used for establishing the same pH in dispersion and blank solution and m (g/L) is the dispersion concentration of adsorbent [31].

Fig. 3 shows the titration curves $Q = f(pH)$ obtained for substrate solution $m = 20, 40$ and 60 g/L at various contact times varying from 16 to 72 h. In all cases examined, the surface charge " Q " is negative for the different contact times, reaching a maximum of 18 in absolute value. The data shows a slight decrease between pH 2 and 3, with an intersection of the curves occurring at $pH = 2$, which indicates an inflection point.

Indeed, for 20 g/L solution, the surface charge increases with increasing hydration time but remains almost constant for a fixed time. However, for 40 g/L and 60 g/L solutions, the surface charge decreases with increasing contact time, in contrast to the observations obtained for the 20 g/L solution. A slight increase in this charge is observed from $pH = 10$ onwards.

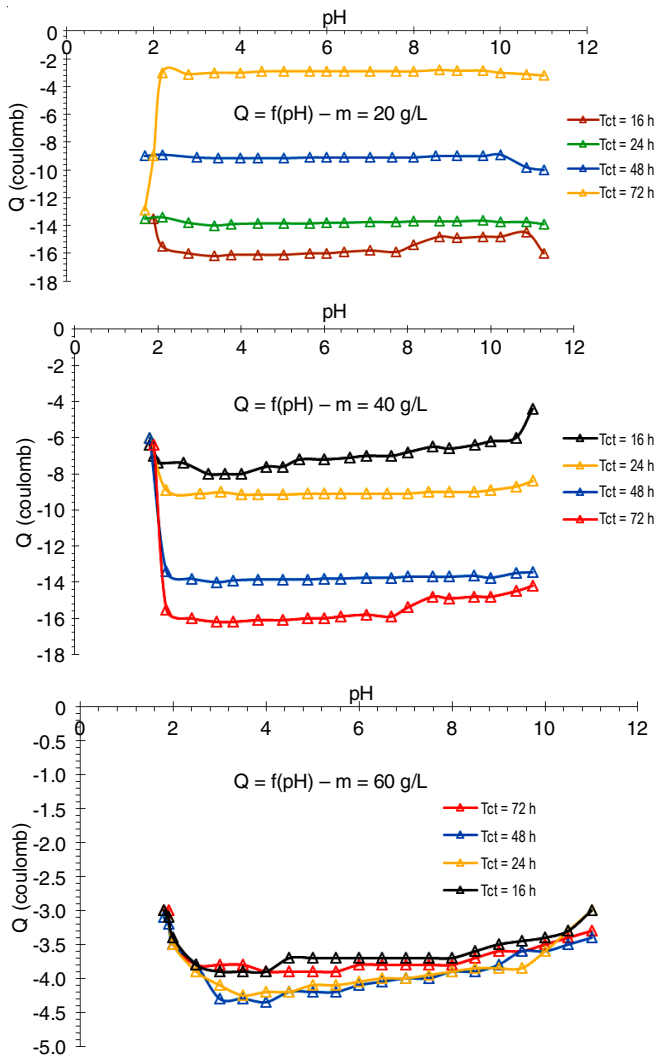
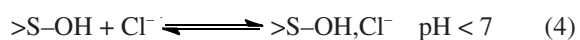
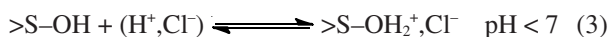


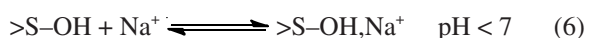
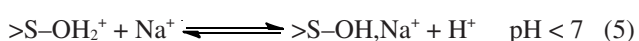
Fig. 3. Variation of $Q = f(\text{pH})$ for 20, 40 and 60 g/L suspension of iron(III) hydroxide in NaCl at different hydration times (T_{ct})

As we have shown, the surface of ferric iron hydroxide has developed a negative surface charge “Q” due to its strong insertions of Cl^- , generally observed at pH values between 2 and 10 and Na^+ ion for pH values above 10. As a result, the permanently charged sites were essentially not involved in any H^+/OH^- exchange reactions over the entire pH range explored. An increase in solution pH led to an increase in the concentration of surface chlorine complexes.

These results demonstrated the existence of a surface ion exchange process at pH values below 10, due to the inclusion of Cl^- . This inclusion of chloride ions with the surface groups $>\text{S}-\text{OH}$ rather than with the groups $>\text{S}-\text{OH}_2^+$.



The sorption reaction of Na^+ agrees with eqn. 1, taking into account that the $>\text{S}-\text{OH}_2^+$ groups predominate in an acidic solution.



As can be observed, surface complexes have been developed due to the insertion of the electrolyte ions, resulting in the following surface complexes: $>\text{S}-\text{OH}_2^+, \text{Cl}^-$; $>\text{S}-\text{OH}, \text{Cl}^-$; $>\text{S}-\text{OH}, \text{Na}^+$.

Conclusion

When investigating the surface chemistry of iron(III) hydroxide, the method employed to ascertain the sorbent characteristics isoelectric point (IEP) and point zero charge (PZC) was to measure the initial pH fluctuations of iron(III) hydroxide solutions as a function of hydration time (T_{CT}). Examination of the plots $\text{pH} = f(T_{CT})$ and their derivative curves smoothed by polynomial equations $d(\text{pH})/d(T_{CT}) = f(\text{pH})$ allowed the deduction of the values of $\text{PZC} = 7.45 \pm 0.1$ and $\text{IEP} = 7.65 \pm 0.1$. The results of variations in the surface charge of $\text{Fe}(\text{OH})_3$ show the existence of a surface ion-exchange process due to the inclusion of Cl^- and Na^+ electrolyte ions. This inclusion, which occurs at alkaline pH, is due to the interaction of chloride ions with $>\text{S}-\text{OH}$ surface groups rather than the $>\text{S}-\text{OH}_2^+$ groups that predominate in acidic solution. The $>\text{S}-\text{OH}_2^+, \text{Cl}^-$; $>\text{S}-\text{OH}, \text{Cl}^-$ and $>\text{S}-\text{OH}, \text{Na}^+$ surface complexes were developed due to the interaction of Na^+ and Cl^- electrolyte ions.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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