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Fe^{2+} adsorption on iron oxide: the importance of the redox potential of the adsorption system

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Abstract
We have demonstrated that the redox potential of the solution containing an inert electrolyte, ferrous ions, and metal oxide allows a much better understanding of the process of Fe(II) adsorption on oxide with the increase of pH. We tested two oxides: γ-Fe_2O_3 (maghemite) and TiO_2 (the mixture of anatase and rutile). For both of them, we determined proton surface charge, Fe(II) uptake curves, electrokinetic potential, and redox potential in solution. The all measured quantities except the last, behaved in an almost identical manner for ferric oxide and titanium dioxide. The redox potential strongly depends on the pH of the solution and stabilizes when the adsorption process is finished (pH above 6). We observed that for the solution consisting only of 0.2 mM Fe(II) and 0.1 KCl the redox potential in the pH range 3–6 can be expressed by the formula: $Eh[mV] = 1120 - 3 \times 59 \times \mathrm{pH} - 59 \times \log(a_\mathrm{Fe(II)})$.

Keywords Redox potential · Ion adsorption · Ferrous ions Fe(II) · Ferric oxide Fe_2O_3 · Maghemite · Titanium dioxide TiO_2

1 Introduction

The redox couple Fe^{2+}/Fe^{3+} is essential for redox equilibria in the environment. In natural waters dissolved iron can exist as Fe^{2+} ion with combination with Fe^{3+} oxides and hydroxides (Stumm and Morgan 1996). Therefore, the reactions between dissolved Fe^{2+} ions and iron(III) oxides were thoroughly studied both experimentally and theoretically (Dixit and Hering 2006; Gorski and Scherer 2011; Gorski et al. 2016; Kerisit et al. 2015; Larese-Casanova et al. 2012; Larese-Casanova and Scherer 2007; Tanwar et al. 2008; Zarzycki and Rosso 2017, 2018).

Experimental investigation of Fe(II) adsorption on metal (hydro)oxides under well-defined conditions is very challenging. Because the oxidation rate of ferrous ions by dissolved oxygen may be very high in the pH range where the adsorption occurs (Morgan and Lahav 2007). All experiments should be conducted inside an anaerobic glovebox in an inert nitrogen atmosphere without any traces of oxygen. All solutions have to be prepared without contact with oxygen which is very cumbersome. So far only a few experimental works have tried to keep these standards [e.g. (Gorski et al. 2016; Nano and Strathmann 2006)].

The measurement of the redox potential of natural waters with the platinum electrode is a standard technique in aquatic chemistry (Pankow 1991; Stumm and Morgan 1996). The results obtained in this way are extremely difficult to interpret without knowing speciation of the solution. In practice Fe^{2+}/Fe^{3+} is one of several redox couples for which we can estimate ions activity ratios because this pair is electroactive on this electrode (Nordstrom 2000).

Several advanced experimental techniques were used to follow Fe(II) adsorption (Gorski and Scherer 2011). Recently, combined potentiometric and electrokinetic measurements were applied to characterized interactions between Fe_2O_3 and Fe^{2+} ions (Toczydłowska et al. 2015). The last study inspired us to apply redox potential measurements to investigate the behavior of ferrous ions in a solution containing different metal oxides.

Nowadays the dominant hypothesis is that adsorption of Fe(II) by ferric and non-ferric oxides has a different mechanism. Fe(II) adsorbed on ferric oxide (like Fe_2O_3) can be easily oxidized by the transfer of an electron from adsorbed species to the solid (Gorski and Scherer 2011; Hiemstra and van Riemsdijk 2007; Larese-Casanova et al. 2012). Fe(II)

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adsorbed on non-ferric oxides (like TiO_2) forms a stable surface complex (Hiemstra and van Riemsdijk 2007; Nano and Strathmann 2006).

We have chosen Fe_2O_3 and TiO_2 to test the above assumptions. In addition to the redox potential measurements, we applied also potentiometric titration, Fe(II) uptake experiments, and electrokinetic measurements. Next, we compared the results obtained for both oxides.

Surprisingly, except for the redox potential, all results for these two oxides were very similar. We have tried to resolve this issue.

2 Materials and methods

So far the majority of experimental work has focused on the most stable iron (hydr)oxides (like hematite and goethite). Maghemite (γ-Fe_2O_3) is rare investigated ferric oxide (Garcell et al. 1998) though is widespread in soils and is responsible for their magnetic properties (together with magnetite) (Barron and Torrent 2002).

In our experiments we used NanoArc iron(III) oxide (maghemite) from Alfa Aesar company (crystal phase gamma, specific surface area in the range of 30–60 m^2/g, particle size in the range of 20–40 nm) and hydrophilic fumed titanium dioxide Aeroxide TiO_2 P 25 supplied by Evonik company (it is a combination of anatase and rutile crystal structures, the weight ratio of anatase and rutile is about 80/20, with specific surface area approx. 50 ± 15 m^2/g. The primary particles have a mean diameter of approx. 21 nm and the aggregates of the particles are several 100 nm in size. The above data comes from the leaflets with information about the products published by suppliers. Both materials used by us have a similar range of surface area—which makes the comparison presented in this study valid.

The solution of the indifferent electrolyte was prepared from KCl salt, and its concentration in most experiments was equal to 0.1 M. During titrations we used standard 0.1 M solution of HCl and KOH. $FeCl_2$ stock solution was prepared from $FeCl_2 \times 4H_2O$ salt using deoxygenated water (obtained by passing pure argon) and hydrochloric acid (the final pH of the stock solution was about 1.2). All used reagents were analytical grade and water had Milli-Q purity standard.

Potentiometric titrations were performed using Metrohm Titrando 907 apparatus. Titration vessel containing 100 mL of a solution was kept in 25 °C by Julabo F12 thermostat and the solution was purged by pure argon (to remove O_2 and CO_2). Combined glass electrode (Unitrode from Metrohm) was applied to measure pH. Unitrode drift limit was established to be below 0.5 mV/min. To monitor redox potential in the solution we used the combined Pt ring electrode (Metrohm No 6.0451.100). The electrode was tested with the redox standard (Metrohm No 6.2306.020) to ensure its accuracy. It was important to clean the surface of the platinum electrode with fine abrasive paste (supplied by the manufacturer) before the series of experiments.

Zeta potential was measured by Malvern Zetasizer Nano ZS with MPT-2 autotitrator. The ζ-potential was calculated from electrophoretic mobility using the Smoluchowski equation (Hunter 1989).

The spectrophotometer (Evolution 201 from ThermoFisher Scientific) was used for quantitative determination of Fe^{2+} applying the colorimetric o-phenanthroline method at the wavelength of 510 nm (Saywell and Cunningham 1937).

The adsorption measurements of ferrous ions were done in titration vessel containing 100 cm^3 of oxide suspension (10 g/L or 2 g/L) in 0.1 M KCl solution with 0.2 mM Fe^{2+}.

After stabilization of pH and redox potential, an aliquot of 400 µL of the suspension was taken. Then the sample was subjected to centrifugation to remove the solid phase. To the received of 300 µL supernatant suitable amounts of reagents were added (hydroxylamine hydrochloride, sodium citrate, and o-phenanthroline) and next spectrophotometric determination of Fe^{2+} was done. The content of the Fe^{2+} ions was checked at the intervals of about 0.3 pH units.

3 Results and discussion

First, we determined the acid-base properties of the metal oxides in solution. From potentiometric titration data of oxide suspension, we could calculate proton surface charge density σ_H:

$$\sigma_H\left[\frac{C}{m^2}\right] = \frac{F}{A_s C_s}\left[\left(\frac{C_{\mathrm{HCl}} \cdot \Delta V_{\mathrm{HCl}}}{V_{susp}} - \frac{1}{\gamma_{\mathrm{H^+}}} 10^{-\mathrm{pH}}\right) - \left(\frac{C_{\mathrm{KOH}} \cdot \Delta V_{\mathrm{KOH}}}{V_{susp}} - \frac{1}{\gamma_{\mathrm{OH^-}}} 10^{\mathrm{pH}-14}\right)\right] \quad (1)$$

where: F—Faraday constant, A_s—specific surface area (m^2/g), C_s—oxide concentration in suspension (g/L), C_{HCl}, C_{KOH}—the concentration of HCl and KOH solutions, ΔV_{HCl}, ΔV_{KOH}—the added volume of HCl and KOH, $\gamma_{\mathrm{H^+}}$, $\gamma_{\mathrm{OH^-}}$—the activity coefficients of H^+ and OH^- ions, V_{susp}—oxide suspension volume.

The above equation follows from the balance of protons and hydroxyl ions in solution and on the oxide surface and it was frequently applied in various forms (Jonsson et al. 2009; Lützenkirchen et al. 2012). The ionic product of water pKw

was assumed to be 14.0 at 298 K which is a standard value in aquatic chemistry calculations (Pankow 1991; Stumm and Morgan 1996).

The activity coefficients were determined from Davies formula (Stumm and Morgan 1996):

$$\log \gamma_i = -A\, z_i^2 \cdot \left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2\sqrt{I} \right] \tag{2}$$

where I denotes ionic strength, z_i is a charge of an ion and $A = 0.5$ at temperature 298 K.

It was assumed that the common intersection point of charge curves (CIP) had to satisfy the condition $\sigma_0(\mathrm{pH} = \mathrm{CIP}) = 0$, so the point of zero charge (PZC) was equivalent with CIP $PZC = CIP$. Because the both oxides had acidic impurities (HCl) deriving from their synthesis process therefore we had to add some amount of acid into formula (1) to took this fact into account and to satisfy the above condition for CIP (Szekeres and Tombacz 2012). In the case of titanium dioxide it was 0.34 ml of 0.1M HCl and in the case of γ-Fe_2O_3 it was 0.57 ml of 0.1 HCl.

From Fig. 1 it follows that the PZC for γ-Fe_2O_3 is equal to 6.9, and the PZC for TiO_2 is equal to 6.6. This last value is in

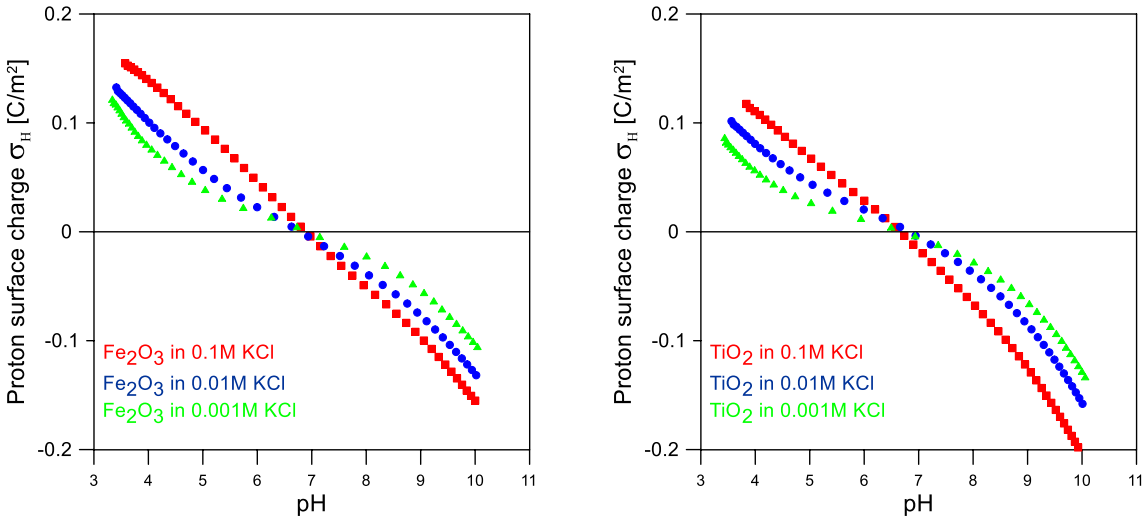

Fig. 1 The proton surface charge of γ-Fe_2O_3 and TiO_2 at three concentrations of indifferent electrolyte 0.1 M (red squares), 0.01 M (blue circles), and 0.001 M KCl (green triangles). The oxide concentration in solution was equal to 10 g/L. The values of PZC correspond to common intersection points of charge curves (CIP) and for γ-Fe_2O_3 PZC = 6.9, and for TiO_2 PZC = 6.6. The surface charge was calculated with the Eq. (1). (Color figure online)

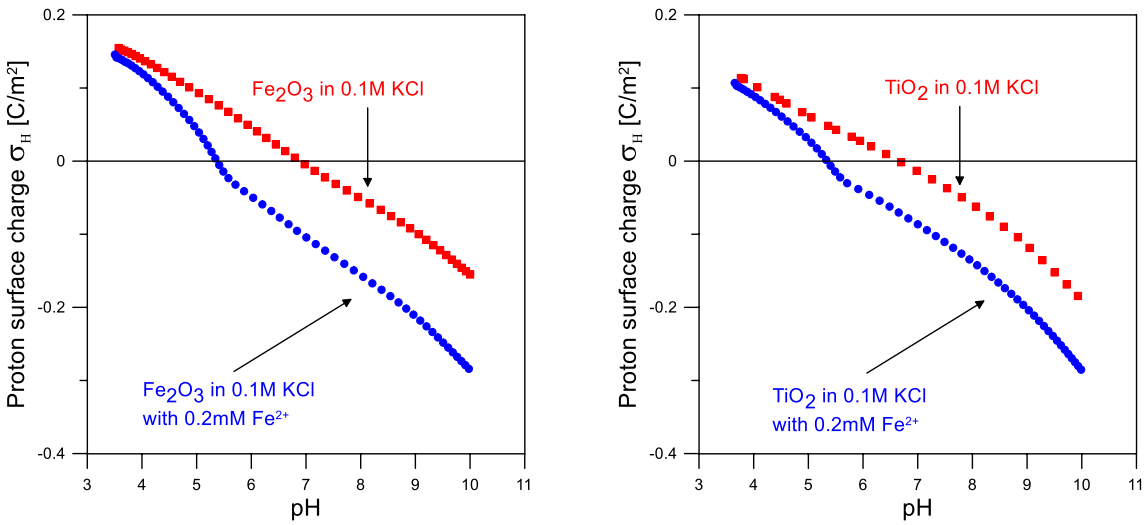

Fig. 2 The proton surface charge for γ-Fe_2O_3 and TiO_2 in 0.1M KCl solution without (red) and with 0.2 mM ferrous ions (blue). (Color figure online)

good agreement with the PZC determined for the same oxide by Szekeres and Tombacz (Szekeres and Tombacz 2012). Also, the PZC for γ-Fe_2O_3 has typical value for this oxide. According to Kosmulski the PZC and IEP of maghemite are at pH 5.5–7.5 (Kosmulski 2016).

In the next experiment, we measured proton surface charge for both oxides in the presence of 0.2 mM Fe^{2+} in 0.1 M KCl solution (Fig. 2). The addition of Fe^{2+} ions shifts charge curves to lower pHs. The course of the curves is very characteristic. First, we clearly observe the deviation of the proton surface charge towards more negative values. At pH 5.5, this deviation stops and the curve runs almost parallel to the original one (without Fe^{2+} in solution). This effect is more pronounced for γ-Fe_2O_3. This may mean that during adsorption of Fe^{2+} ions on iron oxide more protons are released to the solution than in the case of the adsorption of ferrous ions on titanium dioxide. Probably, this phenomenon follows from that the adsorbed ferrous ions on iron oxide surface are oxidized to ferric ions which are next hydrolyzed (Gorski and Scherer 2011; Larese-Casanova et al. 2012).

In order to quantify how many ferrous ions remained in the solution, we applied a classical spectrophotometric method based on the formation of a colored complex of iron ions with phenanthroline (Saywell and Cunningham 1937). Small aliquots of the solution containing iron ions were collected after the system reached equilibrium (i.e., when the glass electrode and the redox electrode gave stable readings—drift below 0.2 mV/min).

First, we examined the system containing only neutral KCl electrolyte and iron ions with a concentration of 0.2 mM (without oxide). For three concentrations of electrolyte 0.01 M, 0.1 M, 0.5 M, we performed titration from pH 3 to pH 7, and at equal intervals of pH, we took aliquots for analysis of the content of dissolved iron.

In Fig. 3 we can see how the detected iron content in the solution changed with pH. For high ionic strengths of 0.5 M and 0.1 M, we observe a mild decrease in concentration in the pH range from 3 to 6. For lower ionic strength (0.01 M), we see that the decrease in iron content is already significant at low pH values. In spite of working in an atmosphere of inert argon, certain amounts of oxygen were present in the tested solution. Fe^{2+} ions under such conditions are oxidized to Fe^{3+} the faster the higher the pH (Morgan and Lahav 2007). Above pH 6 this process rapidly accelerates and probably the insoluble iron (hydr)oxide begins to precipitate. During several minutes the solution turns slightly yellow, and after that one can observe yellow-orange tiny sediment.

The right panel of Fig. 3 shows how the redox potential *Eh* of 0.1 M KCl solution with 0.2 mM Fe^{2+} changes with pH. The values of *Eh* were expressed relative to the standard hydrogen electrode (SHE). For this purpose, the measured redox potential values have been increased by 209 mV (this is the value of the potential of reference silver chloride electrode) (Striggow 2017). We can observe that the experimental points are arranged in a straight line which slope clearly indicates that *Eh* strongly depends on pH.

Assuming that redox half-reaction responsible for the measured *Eh* potential could have the following form:

$$Fe^{2+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ + 1e^- \quad (3)$$

For the above reaction the Nernst equation has the form (Gorski et al. 2016):

$$Eh[V] = E_0 + \frac{2.3RT}{F} \log \left[\frac{\{H^+\}^3}{\{Fe^{2+}\}} \right] \quad (4)$$

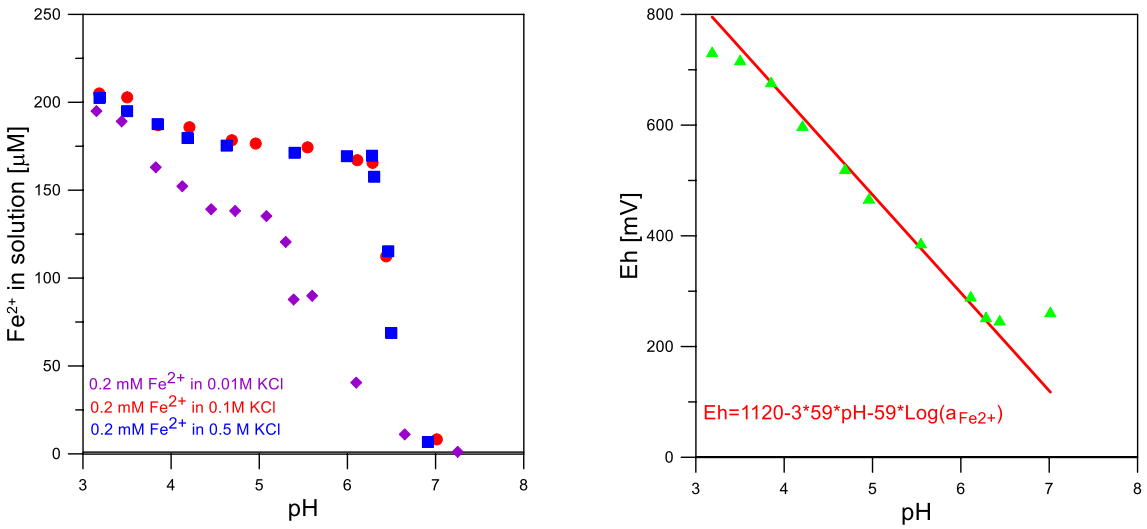

Fig. 3 The concentration of dissolved Fe(II) in solution in different ionic strengths as a function of pH determined by phenanthroline method and the redox potential of solution (green triangles) measured by combined Pt ring electrode for 0.2 mM Fe(II) in 0.1 M KCl solution without oxide. The red line is the regression line defined by the equation inside the panel. (Color figure online)

where curly brackets denote activity. We assumed that $Fe(OH)_3$ is solid, amorphous hydroxide phase for which activity is equal to 1. At room temperature (298 K) we can write:

$$Eh[mV] = E_0 - 3 \times 59 \times \mathrm{pH} - 59 \times \log\left\{Fe^{2+}\right\} \quad (5)$$

We also assumed that the activity of ferrous ions is constant and could be calculated from Fe^{2+} initial concentration and activity coefficient determined from Eq. (2).

Using the formula (5) we fitted the experimental data in Fig. 3 (red straight line) and we found that the parameter $E_0 = 1120$ mV. This value is higher than the theoretical equilibrium potential for the reaction (3): $E_0 = 937$ mV (Gorski et al. 2016). Probably, the determined value of E_0 is a mixed potential of two or more redox processes like the oxygen reduction to water with equilibrium potential of $E_0 = 1230$ mV (compare with Figure 8.28b in the reference (Stumm and Morgan 1996)).

The uptake of Fe^{2+} ions from the solution for two oxide concentration (10 g/L and 2 g/L) is presented in Fig. 4. We have compared uptake curves for γ-Fe_2O_3 and TiO_2 in one graph. It is striking that adsorption edges for two different oxides are almost identical for the both suspension concentrations. The curves for the lower solid concentration are shifted towards higher pHs and have a more bent shape. We would like to remind you here that the dominant opinion regarding the adsorption of Fe(II) ions on oxides is that this phenomenon has a different mechanism for iron oxides and other oxides such as titanium dioxide. For the adsorption of Fe^{2+} on iron oxides, it is assumed that ferrous ions can be easily build up in oxide structure transfering their electrons into the solid bulk (Gorski and Scherer 2011). For titanium dioxide, one assumes that adsorbed Fe^{2+} ions are slightly separated from the oxide surface and form surface-coordinated ferrous ions (Hiemstra and van Riemsdijk 2007).

The uptake curves determined experimentally by us seem to contradict the above assumptions.

However one should remember that despite the apparently similar sorption, the fate of the adsorbed iron may be different in the long-term exposure. In the case of the stable iron oxides, redox-driven recrystallization is observed after days and weeks—and usually only using the isotope tracers (Larese-Casanova et al. 2012).

Comparing our results with the adsorption edges of Fe(II) on goethite (Dixit and Hering 2006) and on titanium dioxide (P25 from Degussa-Evonik) (Nano and Strathmann 2006) which were measured under strict anaerobic conditions we see that iron(II) adsorption on this oxides occur from pH 5 to pH 8. In our case, the adsorption edge starts at pH below 4 and ends at pH about 6–7. It is evident here that the mechanism of Fe(II) uptake from solution is different under anaerobic and aerobic conditions.

In Fig. 5 we can see the redox potential *Eh* measured during adsorption experiments. Initially, the redox potential values decline with pH. The measured values are higher for maghemite than for titanium dioxide. For the lower suspension concentration (2 g/L) the redox potential for γ-Fe_2O_3 firstly follows the *Eh* measured for Fe^{2+} solution without oxide. This changes above pH 5.5, where the redox potential reaches stable value (about 470 mV for both oxides). The stabilization of the redox potential above pH 5.5 follows from that in this region almost all ferrous ions were removed from the solution (compare with Fig. 4).

According to (Zarzycki and Rosso 2017) the fact that iron ions from aqueous and solid phase can exchange at pH 5.5

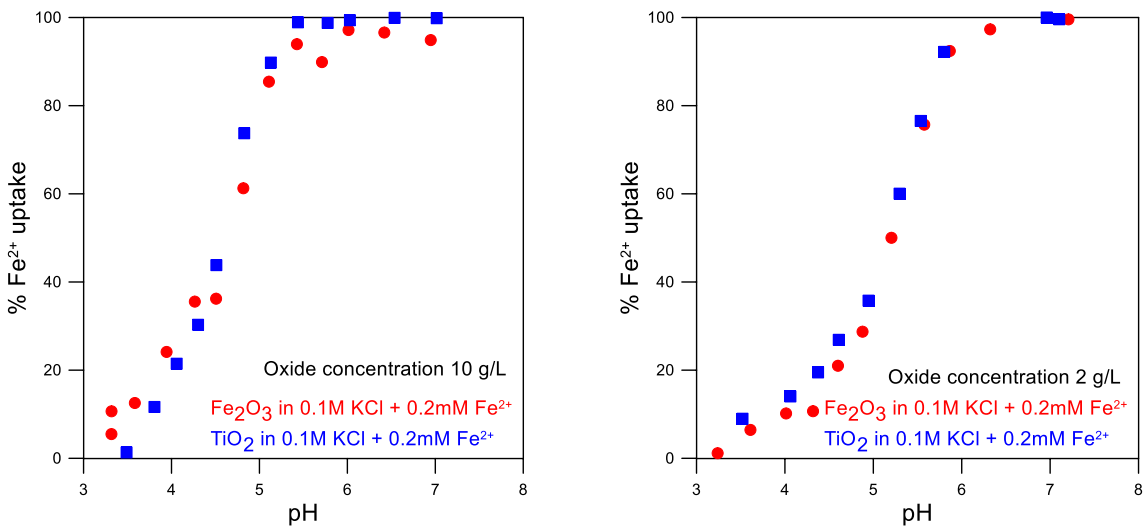

Fig. 4 The adsorption edges of Fe^{2+} on γ-Fe_2O_3 (red circles) and TiO_2 (blue squares) as a function of pH for two concentrations of both oxides (10 g/L and 2 g/L) from the solution that contained 0.2 mM Fe(II) and 0.1 M KCl. (Color figure online)

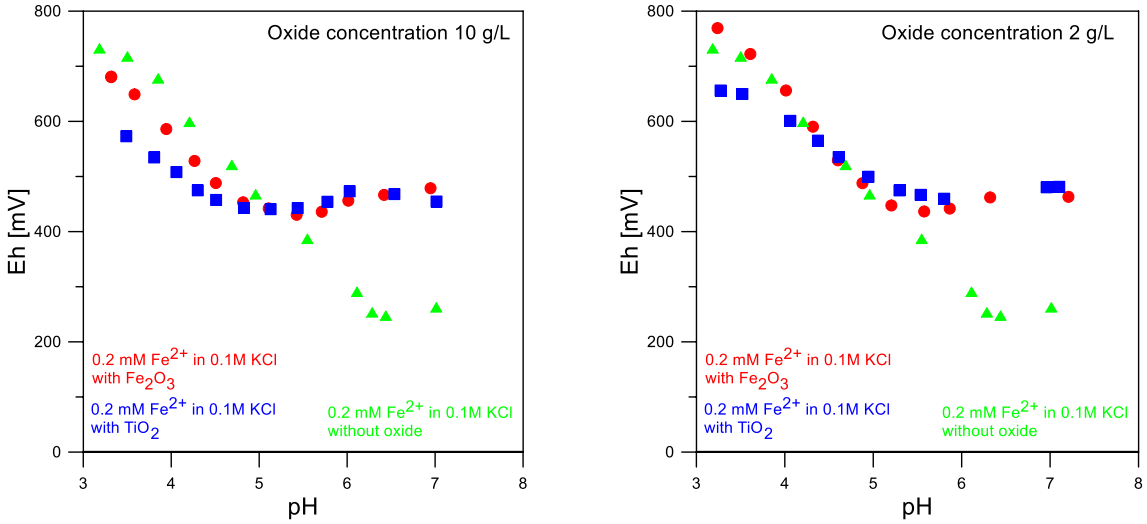

Fig. 5 The redox potential as a function of pH measured for two concentrations of γ-Fe_2O_3 (red circles) and TiO_2 (blue squares) 10 g/L and 2 g/L in the solution that contained 0.2 mM Fe(II) and 0.1 M KCl. Green triangles denote *Eh* measured for the solution without any oxide. (Color figure online)

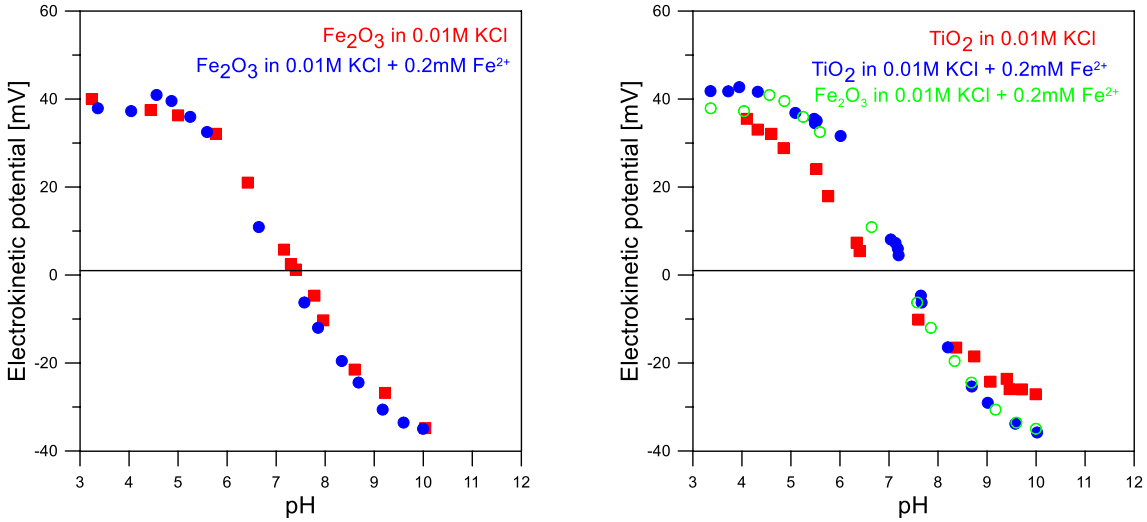

Fig. 6 ζ-potential of γ-Fe_2O_3 and TiO_2 suspensions without (red squares) and with Fe^{2+} ions (blue circles). The IEP of iron oxide in pure 0.01M KCl was equal to 7.5 and in the supension with Fe^{2+} IEP = 7.3. The IEP of titanium dioxide in pure 0.01M KCl was equal to 6.9 and in the suspension with Fe^{2+} IEP = 7.4. We added in the right panel ζ-potential of γ-Fe_2O_3 measured in the suspension containing Fe^{2+} ions (green empty circles). (Color figure online)

is an indirect evidence that Fe(II) from solution has to be adsorbed on the positively charged surface.

The last Fig. 6 presents the measurements of electrokinetic potential (ζ) for oxide suspensions with and without Fe^{2+} ions. During this experiment, the concentration of oxide (γ-Fe_2O_3 or TiO_2) was equal to 1 g/L in 0.01 M KCl solution. The concentration reduction compared to the adsorption experiments was caused by the need to obtain greater accuracy and sensitivity of electrokinetic measurements. It is evident that in the case of the iron oxide there is no difference if the solution contains Fe^{2+} ions or not (isoelectric point (IEP) changed from 7.5 to 7.3—with an error at least ±0.1). In the case of the titanium dioxide, we observe a slight shift of the ζ-potential towards a higher pH (IEP increased from 6.9 to 7.4). In order to keep the charge balance of oxide particles, one has to increase pH to introduce more hydroxyl anions close to the surface of the oxide because Fe^{2+} and K^+ ions adsorbed in the rigid part of the electric double layer of oxide particles. The behavior of ζ-potential for γ-Fe_2O_3 indicates that the adsorption of Fe^{2+} ions on this oxide does not influence on the properties of its surface. It probably means that

adsorbed Fe^{2+} ions on the surface of γ-Fe_2O_3 were oxidized to Fe^{3+} and build into the bulk structure. For this reason, the surface properties of γ-Fe_2O_3 do not change along with the adsorption of ferrous ions. The ζ-potential for TiO_2 with ferrous ions is very similar to the electrokinetic potential for γ-$Fe_2O_3 + Fe^{2+}$ ions. This confirms again that Fe^{2+} adsorption on both oxides gives almost identical results of various measurements.

4 Conclusions

The adsorption of Fe^{2+} ions on metal oxides is a complicated phenomenon. The key factor here is the presence of dissolved oxygen in solution. Under normal laboratory conditions, it is impossible to completely remove oxygen from the investigated system even if we work in an inert gas atmosphere. As the pH increases, the oxygen oxidizes more quickly ferrous ions and produces ferric oxides and hydroxides. This process is competitive in relation to Fe^{2+} adsorption. Measuring the redox potential allows us to follow which process dominates in a given pH range. Under aerobic conditions, ferrous ions adsorption on ferric and non-ferric oxides proceeds in the very similar way. Proton surface charge, adsorption edges and electrokinetic potential (very sensitive for surface properties) cannot distinguish unequivocally which oxide was adsorbent. This means that in the environment the fate of dissolved iron may mainly depends on the properties of solution (pH, temperature, redox potential, oxygen level) and not on mineral composition of soils and rocks.

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