Student's Card 1 Removal of heavy metals from wastewater, e.g. chemical precipitation in the automotive industry

Module Analysis of the precipitation

Introduction

Now we want to analyse our precipitation results and test two possible methods. One uses a certain section of the titration curve as OH^- ions are consumed in the precipitation products, while the other tries to estimate the result by measuring the mass of precipitated particles on the filter. Both methods may differ slightly from the actual value.

Necessities

List of materials/tools

- 4 beakers
- Stir plate
- pH-Meter
- Burette
- Filter 150 mm diameter
- Laboratory balance
- Spatula
- Gloves

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Lab Procedure

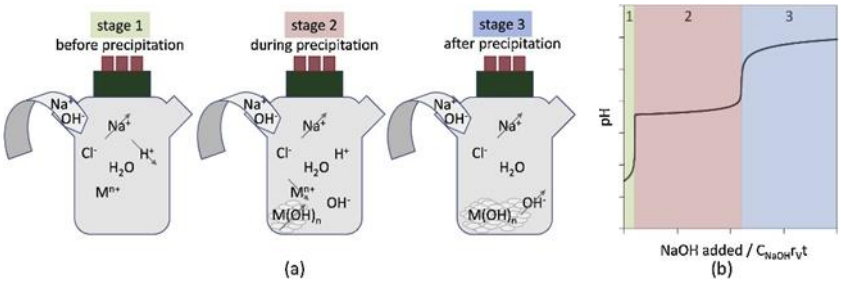

Figure 1 , Source: [1]

Record the total amount of $NaOH$ required for the titration until the end of the experiment.

- The steep slope at the beginning shows the amount of NAOH required to compensate for the free acid, the flat slope from the second inflection point shows the increase in pH per drop of $NaOH$ added in the solution. Why is the curve flat in the middle?

Consider the formula for heavy metal hydroxide precipitation:

$$Me^{z+} + zOH^- \rightarrow Me(OH)_z \downarrow (above\ pH\ 7) \quad (1)$$

For the small amount present as a metal complex in the solution, this conversion pathway is expected upon addition of $NaOH$:

$$[Mn(H_2O)_6]^{2+} \rightarrow [Mn(H_2O)_5OH]^+ + H^+ \quad (2)$$

$$[Mn(H_2O)_5OH]^+ \rightarrow [Mn(H_2O)_4(OH)_2] + H^+ \quad (3)$$

$$[Mn(H_2O)_4(OH)_2] + {}^1/_2\, O_2 \rightarrow MnO_2 \downarrow + 5\, H_2O \quad (4)[1]$$

Consider the effect of this transformation has on the resulting pH?

[1] https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_and_Websites_(Inorganic_Chemistry)/Coordination_Chemistry/Complex_Ion_Chemistry/Reactions_of_the_Hexaaqua_Ions_with_Hydroxide_Ions

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In relation to your experiment, analyse the statement in the following figure:

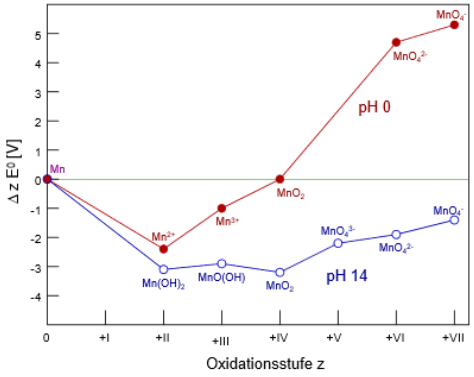

Figure 1 Manganese can be present in a basic environment under electrochemically similar conditions as Mn(II) hydroxide, Mn(III) oxide hydroxide or as manganese dioxide, Mn(+IV) oxide. Source: University of Freiburg, Lecture Chemistry of Metals, Frost diagram of manganese. Online: http://ruby.chemie.uni-freiburg.de/Vorlesung/metalle_mn_gruppe.html

To do this, read off the colour of the different manganese oxides and observe the colour change during the precipitation. You can now make an approximate quantitative determination of the precipitation products in the following way:

1. From the weighed amount of $MnCl_2\ (H_2O)_4$ calculate the potential amount of Mn available for precipitation as $Mn(OH)_2$, $MnO(OH)$ und MnO_2 . Divide the total amount of $NaOH\ in\ mL$ by the number of your individual titration steps (= drops) and multiply this amount by the number of steps that lie between the first and second inflection points of your titration curve. Converted into moles, this should approximately correspond to the amount of OH^- ions "consumed" for the conversion. From this you can determine a possible maximum weight of your precipitates. And you can set the initial amount of Mn in the stoichiometric ratio to OH^-.
2. Weigh a filter with a pore size of 150 mm on an ultra-fine balance and carefully pour your solution with the well-suspended precipitates over the filter. [2] Dry the filter and weigh it again with the precipitates. The difference before and after should be the weight of the precipitate. Due to the various possible reaction products described above, the actual weight may vary depending on their unknown mixing ratios.

Other possible sources of quantitative uncertainty include

- Adsorbed water molecules from the ambient air,
- adhering sodium atoms that have dried out in the filter, and,

[2] A long flow tube should be used for filtration. This will create a slight vacuum as the droplets fall due to the displaced air mass and the solution will flow more quickly from the funnel into the beaker.

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- Since hydroxide precipitation is only the first step in wastewater treatment, in our case we still detected a residual concentration of $0{,}15\ m\frac{mg}{L}\ Mn$ after precipitation, surface loading of the filter with Mn^{2+}ions is also possible.

And there is a further uncertainty arising from two simplifications. No flocculants was used. Finely dispersed solid particles, whether, $Mn(OH)_2\ oder\ MnO_2$ could pass through the filter and "reappear" as manganese in the ICP analysis. The value thus obtained does not necessarily reflect the residual solubility, but may be due to the modified method. In short, the test performed here describes an approximation of the real conditions and the closer one looks at the quantitative values, the more the deviations from industrial practice become apparent under this "microscope".

Figure 3 Precipitation becomes visible from pH 7.5 and reaches a maximum between pH 8 - 9. T=20 °C. F Photo: TU Clausthal

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Figure 4 Filtration with quantitative filter paper, diameter 150 mm. Photo: TU Clausthal.

Calculations

Manganese Ions act as a Lewis acid. Calculate the maximum pH shift due to:

$$Mn^{2+} + 6H_2O \rightarrow Mn(H_2O)_6^{2+} \quad (1)$$

$$Mn(H_2O)_6^{2+} + H_2O \rightarrow Mn(H_2O)_5OH^+ + H_3O^+ \quad (2)$$

$$cMn = cH^+ \quad (3)$$

And compare it, in percentage to the real shift.

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Questions/Quiz

- *Which part of the titration curve can be used to determine – approximately – the amount of manganese Ions precipitated?*
- *What other technique could you use to check the likelihood of this result?*
- *Critically analyse your results. Why are your results inaccurate?*

Sources

[1] Eggermont, S. G., Prato, R., Dominguez-Benetton, X., Fransaer, J. (2020). Metal removal from aqueous solutions: insights from modeling precipitation titration curves. Journal of Environmental Chemical Engineering **8**/1, 103596.

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