Colorimetric Hydrogel from Natural Indicators: A Tool for Electrochemistry Education

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ABSTRACT: The electrolysis of water is popular both as lab work and as a demonstration. In this activity, the electrolysis of water in the presence of a pH indicator is used to produce text and symbols. This report describes the design of an environmentally friendly setup of a writing board utilizing the electrolysis of water in a hydrogel environment. The activity can be performed by only using chemicals and materials that are easily accessible to everyone, with no special permit needed. The writing board has been developed mainly as an outreach activity for our faculty and has been assessed during visits from upper secondary school students.

KEYWORDS: General Public, High School/Introductory Chemistry, Public Understanding/Outreach, Hands-On Learning/Manipulatives, Acids/Bases, Electrochemistry, Oxidation/Reduction

INTRODUCTION

Electrochemistry is an important subject as it is not only very common in everyday life but also important in our society. Its applications can be found in batteries, accumulators, fuel cells, study of the corrosion process, and industrial-scale production of important metals like aluminum.1 Some classic experiments and demonstrations on the subject include writing messages and designing art by exploiting the electrolysis of water.2 Many excellent examples on how to create laboratory work and how to visualize the products using color changes have been published frequently. Some of the examples have used electrolysis of water for demonstrating the chemical composition of water and/or for illustrating the redox reactions using color changes,3–7 while others have developed micro-scale laboratory exercises.8,9

In the electrolysis of water with an inert electrolyte, half-reactions occur at

\[
\begin{align*}
\text{anode} & : 2\text{H}_2\text{O}(\ell) & \rightarrow & \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \\
\text{cathode} & : 4\text{H}_2\text{O}(l) + 4e^- & \rightarrow & 2\text{H}_2(g) + 4\text{OH}^-(aq)
\end{align*}
\]

The electrolytic products including H⁺ and OH⁻ from eqs 1 and 2, respectively, show why pH indicators are a natural choice for illustration of the redox reaction. Examples of indicators used for this purpose include bromocresol green, bromothymol blue, and thymolphthalein.4,6 Another popular natural pH indicator is the juice of red cabbage due to its nontoxicity and broad changes in color. It is commonly used in Finnish schools, especially for the lower grades.10,11 The reason for the changes in color with pH are anthocyanins, the compounds that are present in red cabbage as well as in blueberries. The anthocyanins in red cabbage will change their color depending on pH of the environment such as a green at highly alkaline, blue at slightly alkaline, purple around neutral, pink at slightly acidic, and red at highly acidic conditions.11

Experiments in liquid media often require careful handling and uncontrollable contour of products; thus, gelatin and agar have been used to prepare hydrogels for electrochemistry by both Stauffer and Fox6 and Davis et al.8 Another interesting group of compounds for making gels are carrageenans, natural polysaccharides that can be extracted from red algae, some of which can be found also in parts of the Baltic Sea. Carrageenans are common in everyday life as they are used as stabilizers, thickeners, and gelling agents for example in the food industry. Aqueous solutions of carrageenans with specific cations will form physically cross-linked polyelectrolyte gels, that are thermoreversible.12–14

In this work, we have combined the teaching of pH and electrochemistry inspired by reported methods from

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others,\textsuperscript{2}–\textsuperscript{11} focusing here on showing the wonders of everyday chemistry. In this paper, we describe the design of an environmentally friendly setup of a writing board utilizing the electrolysis of water in a hydrogel environment. The concept of using electrochemistry for producing text has been reported by others.\textsuperscript{2,13,16} The emphasis of the method reported in this paper has been on the electrolysis of water with the key factors being a safe and environmental friendly experiment. The reactions both at the cathode and at the anode can be performed without any special equipment, space, or ingredients. The setup has been developed for school visits to our Faculty of Natural Science and Engineering at Åbo Akademi University. Our aim is foremost to introduce chemistry in a fun and surprising way, showing that chemistry is present in our everyday lives and does not have to be dangerous. We have also taken this as an opportunity to show that chemistry does not have to be just test tubes; it is so much more and can also be a form of art. As an additional experiment, we also demonstrate how the hydrogel can be used for making stencil pictures.

\section*{DESIGN}

\subsection*{Materials}

Reagent grade K-carrageenan, anhydrous magnesium sulfate, and ammonium hydroxide were acquired from Sigma-Aldrich. Reagent grade hydrochloric acid was acquired from Merck. K-carrageenan (SpecialIngredients) for cooking purposes and Epsom salt (magnesium sulfate, Nortembio) were bought through Amazon but are also available through pharmacies and health food stores. Red cabbage (\textit{Brassica oleracea}), bilberry (European blueberries, \textit{Vaccinium myrtillus}), vinegar, citric acid, baking soda, and 9 V batteries were all purchased from a local supermarket. Petri dishes (d 90 mm) were acquired from VWR. The copper wire was bought from a local hardware store.

\subsection*{Hazards}

All materials used in the writing board experiment are nonhazardous. For the stencil pictures (additional experiment), strong acids and bases are used. Proper lab safety measures should be taken, including working in a fume hood, wearing a lab coat, and using gloves and glasses.

\subsection*{Preparation of pH Indicator Juice}

Red cabbage and bilberry juices are chopped and crushed respectively after which newly boiled water (from a water boiler) is poured over and the mixture is left standing for an hour. To remove the solid pieces, the mixture was poured into a flask using a coffee press. For the red cabbage juice, we used 1200 mL of water and 450 g of chopped fresh red cabbage. For the bilberry juice, we used 1200 mL of water and 300 g of frozen bilberries. To have the juice readily available, a large batch can be made and stored in the freezer.

\subsection*{Preparation of the Responsive Hydrogel}

To produce the hydrogel, 1.5 wt % of carrageenan is added to a 0.09 M solution of magnesium sulfate consisting of 60\% 0.15 M magnesium sulfate solution and 40\% indicator juice (prepared as described above). The carrageenan is added slowly and carefully under stirring and heating (70 °C). Care should be taken so that no clots, especially big ones, of carrageenan are formed. The pH of the solution can be adjusted using vinegar, citric acid, or baking soda in order to get the desired color of the gel. When all the carrageenan has been added, the solution can be removed from the heating plate. Upon cooling, the solution forms a hydrogel, and the hydrogel can be stored for more than a week in the fridge.

\subsection*{Preparation of the Writing Board}

For writing purposes, the hot (70 °C) solution should be poured into a dish with low edges but a fairly large area (e.g., a Petri dish). The electrode setup for writing includes a ring of copper wire as the anode and copper wire as the cathode setup of the experiment as introduced to the visiting students (9 students; Figure 1). The writing is done by attaching the copper wire in the hydrogel to one terminal of a 9 V battery while attaching another piece of straight copper wire (cathode) to the other terminal. We have used the negative terminal for writing as shown in the pictures in Figure 1. The straight copper wire is used as the pen; by making a small bend at the end, one can write by applying it gently and therefore without destroying the hydrogel. We have made copper pens by removing everything but the shell from a ball point pen and sticking the wire through it (Figure 2 and Figure S2, Supporting Information); detailed instructions can be found in the Supporting Information. The hydrogel can be used after a few hours but will work much better if left overnight at room temperature. The firmer the hydrogel is, the better the writing will be. If care

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic three-step assembly and use of the writing board: (I) copper wire and Petri dish, (II) copper wire and pH indicator gel in Petri dish, and (III) final assembly of the writing board, with copper wire used as a writing tool attached to the negative terminal of the battery and copper wire in the gel attached to the positive terminal.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{(A) Design of our copper pen used as the tools for writing by visiting students, in the picture attached to an alligator clip. (B) The setup of the experiment as introduced to the visiting students (9 V battery, copper pen, alligator clips, pH indicator gel with copper wire).}
\end{figure}
is taken not to overheat the hydrogel, it can be reused after
careful heating and stirring.

■ EXPERIMENTAL PROCEDURES

Writing Board Experiment

As mentioned in the Introduction, we have used our writing
board when presenting the subject of chemistry at Åbo
Akademi University to visiting upper secondary school
students. The concept of the writing board has been
introduced to the students as a challenge with three tasks:

- Can you write your name in the hydrogel in such a way
  that scratching the gel is not your main form of
  producing the letters?
- How many different colors can you produce in the
  hydrogel?
- Can you tell which terminal of the battery you have used
  for writing?

The clues given for the task are eqs 1 and 2, and a colored
pH scale for red cabbage juice along with a list of the materials
available. For the purpose of the last task, the terminals of the
battery are hidden beneath duct tape. A more detailed
description can be found in Figure 2. Figure 3 and Figure S3
(Supporting Information) shows text produced using the
negative terminal of the battery.

Additional Experiments with the pH Responsive Hydrogel

Our main purpose for the hydrogel is using it as the presented
writing board. Where electrochemistry has been used by others
for writing messages, the pH reactivity of red cabbage has been
used to make art in the form of patterns and paintings.17,18 To
add to the versatility of the hydrogel, we have also used it as a
substrate for making stencil pictures by exposing it to gases;
examples of stencil pictures can be seen in Figure 4. The
stencils used for the pictures presented here were made using
paraffin. Using the stencils, the hydrogel was exposed to acidic
or basic gases according to the desired color. For the included
examples, we have used hydrochloric acid (red) and ammonia
(green/yellow) (see also Figures S4 and S5, Supporting
Information). The stencils can be made by students, but the
gas exposure, which must be done in a fume hood, should be
left to the teacher and only after taking proper safety
precautions. The hydrogels should also be left in the fume
hood for a while after the exposure. Since we have a hydrogel,
the gases will easily penetrate and dissolve into the hydrogel,
causing the color change. The ability to absorb additionally
added water is not as good or as fast as that of paper.
Therefore, you will not have results that are as nice by trying to
paint with acid—base solutions. However, it gives instructors
the opportunity to introduce another type of technique.

■ INTEGRATING THE ACTIVITY INTO THE
CURRICULUM

This activity can be part of an outreach activity and can also be
integrated in the classroom on different levels as it combines
many different concepts, for example, acids/bases, indicators,
and electrochemistry. The concepts dealt with in the lab work
make it suitable for both lower and upper secondary school in
accordance with the Finnish curriculum for chemistry
education. Something that is also highlighted in the Finnish
curriculum is the importance of building a sustainable future,
as this lab work builds on the ideas of biodegradability and fits
well also with this important subject.

■ EVALUATION

The experiment has been tested with 33 students from three
different schools. After being introduced to the concept and
finishing the three tasks mentioned earlier, the students were
asked to evaluate their experience with the writing board. The
students were asked about their earlier experiences with the
electrolysis of water and about their opinions regarding the use
of the writing board. Some questions had been left unanswered
by some of the students, and some had filled in the form as a
pair. The survey of their earlier experience with electrolysis of
water was evaluated with yes or no questions. The survey
regarding their opinions of working with the board was
evaluated using open questions. The results of the survey can
be found in Figure S5A,B, where the answers to these open
questions could all be categorized as being either “yes” or

Figure 3. Red cabbage and bilberry hydrogels before and after writing
“ÅA” using electrolysis.

Figure 4. Pictures of (A) letters “ÅA” and (B) random art made using
stencils and exposure to hydrochloric acid (resulting red color) and
ammonia (resulting green color) gases.

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"somewhat". Some answers to the question “Other comments?” can be found in Box 1.

![Figure 5. Results of the questions regarding (A) earlier experience of the electrolysis of water and (B) the open questions about the experience of using the writing board.](image)

| Were you familiar with the electrolysis of water from before? |
|-------------------------------------------------------------|
|               | 0%  | 20% | 40% | 60% | 80% | 100% |
| As a demonstration | 14  | 15  |     |     |     |     |
| As labwork       | 7   | 21  |     |     |     |     |
| Using indicator, as demonstration | 8   | 21  |     |     |     |     |
| Using indicator, as lab work | 7   | 21  |     |     |     |     |

| Opinions about the writing board |
|----------------------------------|
|               | 0%  | 20% | 40% | 60% | 80% | 100% |
| Did you like the concept of the board? | 18  | 0   |     |     |     |     |
| Was it an interesting way of presenting chemistry? | 24  | 1   |     |     |     |     |
| Did you understand what you were doing | 17  | 3   |     |     |     |     |
| Did you learn anything? | 21  |     |     |     |     |     |

### DISCUSSION

There are multiple reasons regarding why we have chosen to use natural pH indicators and carrageenan. One of them is the opportunity to show the chemistry that is all around us. Choosing food items makes the experiment nontoxic, biodegradable, and environmentally friendly. In addition, it is also cost-effective both when it comes to purchase and waste handling. The average cost for a 1 cm thick hydrogel made with commercial chemicals in a 90 mm Petri dish, including the copper wire, is 0.28 euros. The Petri dish is not included in the price, nor is the battery. Most importantly, this makes the experiment accessible not only for teachers without a laboratory (e.g., in elementary school) but also for students who want to continue the experiment at home. We have chosen to use magnesium sulfate for the same reasons as we have chosen the other components. It is inexpensive, nontoxic, biodegradable, easily obtainable, and easy to handle, even though sodium sulfate is more commonly used for the electrolysis of water especially when pH determination is also important. The magnesium ion (Mg²⁺) also enhances the gelation of the carrageenan compared to the sodium ion (Na⁺). An increasing concentration of Mg²⁺ will, however, decrease the hardness of the hydrogel. Other gel-based electrolysis setups have been seen in this Journal earlier, using gelatin-based gels, both for illustrating color changes and for making macroscale setups. Our hydrogel can be utilized also for these kinds of experiments and works well for a color changing reaction as it is highly transparent in its native form (i.e., without indicators present).

The visiting groups are usually very diverse, regarding both interest in and knowledge of chemistry. Some are very interested and have solid knowledge; others lack interest and have difficulties even with very basic concepts. This means that some students need more help than others; we have still decided not to give too many recipe-like instructions. Instead, we have made sure to have enough instructors present to enable discussion for those who need help. This also gives the instructor the opportunity to meet the students at their level. Suggestions for strategies on how to help the more unprepared students can be found in the second Lab Work heading (Lab Work for Classroom—Writing Board) in the Student Notes portion of the Supporting Information, as this work has been developed on the basis of our discussions with the visiting students. The laboratory time for our visiting groups varies between 30 and 60 min, with 30 min being the more common option. Due to the short time, we usually have very little time for further discussions. However, with more time on one’s hands or if someone is using this in a classroom setting, we see this as a great opportunity to take the demonstration further by discussing topics like green chemistry and the need for reducing waste, especially hazardous waste. The Petri dish used in the experiment, whether it is plastic or glass, can and should be cleaned and reused in other experiments. Plastic as a material has gained a lot of negative publicity in recent times and can be exchanged for something more recyclable like a drink carton. The battery can be exchanged for a small hand driven motor or solar cell.

We have used this experiment as an outreach activity for upper secondary students. However, it is possible to use it also with younger students as a more structured activity with more specific instructions. In this case, we recommend to at least start with using the cathode (the negative terminal of the battery) for writing as this reaction gives a much quicker response. The instructions for the outreach activity are based on limited time resources. We have noticed that some of the students are struggling with basic concepts, so we have therefore also developed instructions for classroom settings based on our experiences with the visiting students. These can be found in the Supporting Information.

The positive outcomes of combining science and art, as well as the benefits of using everyday items, have been addressed by several authors. Our overall impression is that, also, the students we have encountered really enjoyed both the artistic elements and the freedom of creativity of the experiment very much.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.0c00440.

Notes for instructors, including more detailed instructions on how to prepare the gel; additional photographs of the gel and the setups; and student notes for two versions of the writing board experiment (PDF, DOCX)

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Notes
The authors declare no competing financial interest.

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