DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY
CHEMISTRY 3411, FALL 2018
AQUATIC CHEMISTRY

Instructor: Professor Brian J. Majestic
Office Phone: 303-871-2986
Email: brian.majestic@du.edu
Office: SGM Room 151
Cell Phone: 480-204-9515
Office Hours: announced in class

Course Description: This is a course in *aquatic chemistry*. We will examine the chemical processes which dominate natural waters in oxic and anoxic environments in the earth system. We will discuss basic properties such as alkalinity and then move to advanced topics such as red-ox equilibria, chemical equilibria of multiple components, and solubility as a function of pH. In a small laboratory component, we will tackle a real problem dealing with the remediation of heavy-metals in drinking water. A common theme of this course will be to understand how the chemistry of the system can help to dictate water quality, as well as water treatment for drinking water.

It is assumed that you have a sound knowledge of general chemistry and a good understanding of the concepts of equilibrium. Of most importance is a good handle on Analysis of Equilibrium Systems (CHEM 2011) or Quantitative Chemical Analysis (CHEM 2270), as Aquatic Chemistry is a direct extension of many of the concepts covered there.

Textbooks: There is one textbook listed for this course. There are required readings from this textbook, and I highly suggest obtaining a copy. This is a relatively basic textbook, and I will provide supplementation as needed.

- Manahan SE; *Water Chemistry,* 2011, CRC Press, ISBN: 978-1-4398-3068-0

I will also be drawing off of the following textbook, although it is not necessary to purchase:

- Stumm W and Morgan JL; *Aquatic Chemistry: Chemical equilibria and rates in natural waters*, 3rd Ed, 1996, John Wiley & Sons, ISBN: 978-0-471-51185-4

Other Resources: In addition to the textbook, lecture presentations, and handouts, you will have the opportunity (and requirement) to consult other resources. These will consist of websites (laboratories, trade associations, government sites, user groups, and list-servers), electronically available journals, and paper-based journals. Most journal articles published 1970-present are available in electronic format and may be printed and/or stored in journal publication format as *.pdf format. Two examples of where to look are as follows: A) the ACS journals (pubs.acs.org) are available from any DU-based URL; and B) many other journals are available free of charge from several databases available at the DU Library website (www.library.du.edu/). The most useful databases are A) www.sciencedirect.com, "Sciencedirect", a service with > 1000 full-text journals which the DU library subscribes to, and B) the Web of Science, which can be accessed directly from the Penrose Library webpage (search the Databases at http://library.du.edu/site/). All of the library databases are available without a personal account from any campus-based URL; however, you can access them from off-campus through the DU library's website with proxy identification.

The University Libraries Research Center answers research questions seven days a week by phone, email, in-person, chat/IM or text. One-on-one research consultations in the Anderson Academic Commons are also available on a drop-in basis or by appointment. Consultations help students at any stage of the research process, from refining a topic, to finding books and articles, to creating a bibliography with RefWorks. Ask a question or make an appointment at 303-871-2905 or research-help@du.edu.

Course Topics

I. Introduction / bulk properties (~ 1 week)

- *Hydrological cycle*
- *Importance and anomalies of water*
- *Bulk properties of water – alkalinity and acidity*
- *Charge balance*
- *Activity*

II. Acid-base chemistry (~ 2 weeks)

- *Carbonate Equilibria*
- *Multiple components*
- *pC – pH diagrams*

III. Red-ox equilibria (~ 2 weeks)

- *Importance of oxidative and reductive environments in aquatic waters*
- *Free energy and its relation to red-ox reactions*
- *The "power" of an electron: metal speciation and pE-pH diagrams (Pourbaix diagrams)*

IV. Water Treatment Processes (~ 1 week)

V. Student Presentations (see details at the end of the syllabus) (1 week)

Note that this class is not a prerequisite for any further classes. Therefore, this schedule is ***extremely*** flexible. If you want to go deeper into a topic currently under discussion or if there is a general consensus that we should skip something so we can get into other topics, then say so!

Evaluation Methods

Over the 10 week quarter, you will be evaluated by several criteria. Specifically, you will be expected to complete the following:

- 2 in-class exams – the 2^{nd} will be during the Final Exam period and is cumulative.
- Sporadic homework (3-4)
- 1 laboratory report (in groups) (see end of syllabus).
- 1 **paired** presentation 20-22 min (+3-5 min questions) presentation, including a written report, described in detail at the end of the syllabus.

In the event that you must miss an in-class exam, please let me know ASAP (in advance if possible) and a makeup will be scheduled. I am generally reasonable, but reserve the right to deny makeup exams for confabulated reasons, in which case your missed exam will be counted as a zero.

The breakdowns, immediately below, reflect the “default” grading distribution. As with everything in life, **this is negotiable.** If you believe that you would perform better with different weightings, then we can meet in-person to discuss this by **Tuesday, Sept 18**.

* Summary of evaluation:

Exams (2 x 20)	= 40 %
Homework	= 15 %
Individual Project	= 25 %
Laboratory Project	= 20 %

A	≥ 93 %	C	≥ 69 %
A-	≥ 90 %	C-	≥ 65 %
B+	≥ 87 %	D+	≥ 62 %
B	≥ 83 %	D	≥ 58 %
B-	≥ 80 %	D-	≥ 54 %
C+	≥ 74 %	F	≤ 54 %

I reserve the right to make downward adjustments to this scale (i.e. adjustments in the direction of leniency). In no event will the actual scale used be adjusted upward from that described above.

Important Dates:
Sept 10: Classes begin
Sept 16: Last day to drop for 100% refund and drop deleted from record
Oct 21: Last day to drop without approval (W assigned)
Fri, Nov 16: Last day of classes
Tues, Nov 20: Final Exam 08:00 – 09:50, Olin 103

Paired Project:

In the last week of this course, you will lead a 20-22 min (+ ~3 min Q/A) discussion. In addition, a **3-5 page** (title page and references excluded) report of your findings will be turned in on the date of your presentation. Technical details of the report are below:

- Double spaced
- 12 pt Times New Roman **or** 11 pt Arial
- 1” x 1” margins (this is NOT the default in MS Word).
- Need **at least** five references, only **two** of which can be from reputable web sites. The others must be primary research articles. In general, a “.gov” site is OK (EPA, USGS), in addition to some international agencies such as UNEP and the WHO. Some “.com” sites may be OK, but talk to me if you have questions about the integrity of a specific site.

Please be prepared to lead the class for your presentation. Here are some tips for a successful discussion:

1. You are free to use slides, powerpoints, demonstrations, skits, or anything else which will help the class learn the material. Feel free to have an interactive portion, as well.
2. This is not a trivial task – I suggest that you start your research at the beginning of the quarter.
3. I am happy to meet with you as much as you’d like for consultation. However, you are **required** to meet with me at least **twice** during the quarter.

Relevant Dates for the Special Project:

- Tues, Sept 18: Turn in one piece of paper for your topic (see below). This paper should contain 1) your name and 2) your preferred topic + one back-up topic.
- Thurs, Sept 20: I will approve your choice or suggest an alternative (in class).
- Friday, Oct 5: Deadline for Meeting #1: progress of research and obtaining references
- **Thurs, Oct 25: Rough draft of paper due with bibliography**
- Thurs, Nov 1: Deadline for Meeting #2: will discuss rough draft and upcoming presentation
- Nov 13 and Nov 15 – Presentations

Ideas for topics (there are many others and *original ideas are certainly encouraged*!!)

- Water quality and treatment in underdeveloped countries
- Isotope dating and tracing of aquatic organisms
- Ocean acidification
- Iron ocean fertilization
- Pharmaceuticals in drinking water – source and treatment
- Engineered metallic nanoparticles in drinking water
- Desalination of seawater
- Mercury pollution and poisoning
- Fluoride removal
- Microplastics
- Coastal algae blooms
- Phytoremediation (i.e., plants and trees to clean water)
- Other (specify)

Project grade break-down (100 pts total):

Preparation (5 *pts*)

Meeting #1 (prior to end of Oct 5) (2.5 *pts*)
Meeting #2 (prior to end of Nov 1) (2.5 *pts*)

Two multiple choice questions (with answers) for Exam II (5 pts)

Presentation (45 pts)

Content (*25 pts*)

Appropriate scope (5 *pts*)
Relevant and correct chemistry/concepts (*10 pts*)
Summary/Conclusions (2.5 *pts*)
Answers to questions (2.5 *pts*)

Form and style (*20 pts*)

Slide quality (uncluttered, clear) (*5 pts*)
Clear explanations (5 pts)
Verbal quality, eye-contact, body-language (*5 pts*)
Timing (*5 pts*)

Written report (*40 pts*)

Appropriate **introduction** of the problem/topic (8 pts)
Appropriate **level of research** into the problem/topic (12 pts)
Independent **conclusions** based on research (10 pts)
Grammar/spelling (5 pts)
References (5 pts)

Peer Evaluation (10 pts)

Laboratory Project

Lead in drinking water

Motivation:

Lead is a heavy metal, considered toxic to humans at any level > 0 ppb (EPA) due to the fact that it bioaccumulates. For drinking water, the EPA maximum contaminant level (MCL) is 15 μg Pb L^{-1}, or 15 ppb. The MCL goal (MCLG) is 0 ppb, although this is non-enforceable. The recent situation uncovered in Flint, MI where concentrations were measured as high as **1,000 ppb** right out of faucets in residential areas (Flint Water Study Updates). This is primarily due to the corrosive nature of the drinking water (high chloride) leading to its ability to degrade lead-containing pipes. This has obvious implications on the health and well-being of people drinking the water, particularly affecting children (born and unborn), as well as pregnant woman (premature birth).

Objectives:

a) To determine reasonable removal mechanisms for Pb from water
b) Determine if the water treatment should take place at high (9000 ppb) or low Pb concentrations (30 ppb)?

Overview of method:

The class will work in **groups of 2-3 (5 groups)** and each group will test a different sorbent for Pb removal at various concentrations. We will test the ability of ~ micron sized particles to act as a sorbent to remove Pb from water. The particles to be tested are:

1. Two types of clays
2. Hematite (Fe_2O_3)
3. Activated carbon
4. Silica

The lab should require 2 full class periods. During these lab periods, we will vary the Pb concentration in **pure water** to determine where the greatest removal efficiency lies. In the end, the class will pool their data and we will determine which sorbent most effectively removes Pb from solution at various concentrations and ionic strengths. Most of the lab work will occur in Dr. Majestic's research laboratory (SGM 143) and we will use inductively coupled plasma – mass spectrometry (ICP-MS) to measure the Pb concentrations. Because this is not an instrumental analysis course, you do not need any prior knowledge about the technique. However, you will learn your fair share after completion of this lab.

Details of method:

Due to the toxicity of Pb, Dr. M will prepare a diluted solution (2000 ppm) of Pb for use. Dr. M will also prepare calibration standards for the instrumental analysis. This method is divided into "Weeks" and will take 2 class/laboratory periods.

1. Preparing the experiment:

    a. Prepare 7 vials of 5 g L^{-1} sorbent (total volume will be 40 mL).
    b. Add about 20 mL of high-purity water (this value does not have to exact, at this point).
    c. Label each vial as 0, 30, 100, 300, 1000, 3000, and 10000 ppb and add the correct amount of 2000 ppm Pb stock solution to get to that concentration.
    d. Fill each vial to the 40 mL line with high-purity water
    e. Put on shaker or rotator and let sit until next lab period.

2. Analysis of samples

    a. Bring all of your samples to room 267 SGM (Dr. Margittai's research lab). We will be using the centrifuges to separate the sorbent from the rest of the solution (details provided that day). Some may need filtration instead…
    b. **Carefully** (do not mix/agitate) pipet exactly 3 mL of the **supernatant** into a clean, labeled 15 mL analysis vial.
    c. Add 15 µL concentrated nitric acid (**ask for help** if you have never used a micropipette). This will bring the solutions to 2% HNO_3, which is necessary for analysis by ICPMS. You will have to take account for this small dilution in your data analysis.
    d. Dr. Majestic will give a brief overview of the technique and we will proceed with sample analysis by quadrupole ICP-MS.

This will complete the experimental part of the lab. You next step is to calculate the "removal efficiency" of each sorbent at each concentration. In other words, how much Pb was left in the supernatant of the total? If 1 ppb was left from your 100 ppb Pb solution, then you have a 99% removal. Make a graph of "removal efficiency" vs "Pb concentration." We will discuss, in more detail, adsorption mechanisms and theories which will aid you in your data work-up.

Again, the data will be pooled so that everyone has access to everyone's data. The reports are handed in in groups and should follow the format of a scientific article (e.g., see Environmental Science & Technology).

1. An introduction of the problem you are trying to solve / address
2. Overview (not the details) of methods used to address the issue
3. Results: provide your adsorption curve and values of K_d.
4. Observations – what did you learn? What sorbents worked best in pure water? What concentrations were the "sweet spot?" This is where you can present figures. At the minimum, you should have at least one figure "% removal vs Pb conc," **and** your adsorption isotherms. More are helpful, as needed.
5. Discussion: **Why** did different sorbents have different removals (if they did?)?

Rubric for Report (out of 100):

Introduction: 15
Methods: 10
Data work-up and calculations: 30
Observation/Interpretation: 10
Discussion of sorbent properties: 25
References: 5
Grammar: 5

References:

https://www.epa.gov/your-drinking-water/basic-information-about-lead-drinking-
http://flintwaterstudy.org/2015/12/complete-dataset-lead-results-in-tap-water-for-271-flint-samples/