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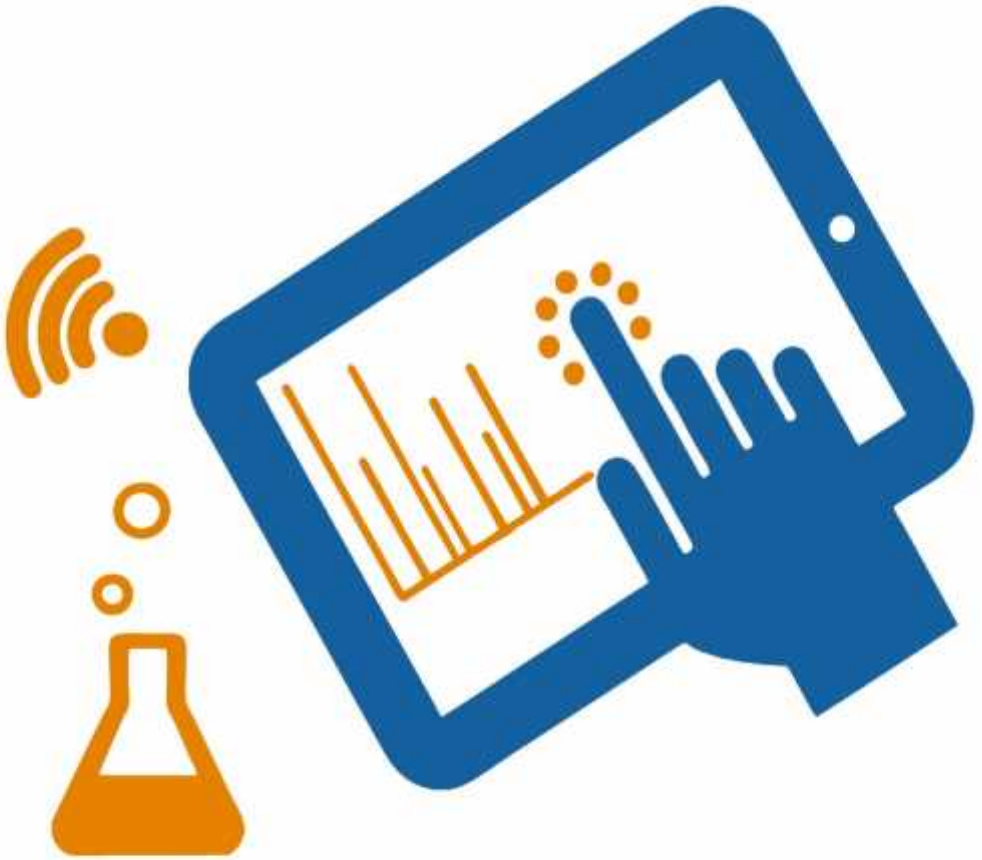

NETCHEM

Application of new biosorbent based on chemicaly modified Lagenaria vulgaris shell for the removal of copper(II) from aqueous solutions

Miljana Radovic

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NETCHEM Remote Access Laboratory Guide

Application of new biosorbent based on chemicaly modified *Lagenaria vulgaris* shell for the removal of copper(II) from aqueous solutions

In this exercise, you will:

- Measure the appropriate amount of $Cu(NO_3)_2$ and make a standard solution and working solutions,
- Measure the required amount of biosorbent needed for treatment,
- Perform experiments in batch conditions,
- Samples taken at certain time intervals analyzed on the atomic absorption spectrometer,
- Analyze the results obtained by atomic absorption spectroscopy on the basis of already acquired knowledge.

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Background

Toxic heavy metals are released into the biosphere through industrial activities and spread into the environment. Their presence in the environment can be detrimental to people, plants and animals. They can accumulate in water, soil, plants and living tissues, thus becoming concentrated throughout the food chain.

Copper is widely used in electrical wiring, plumbing, gear wheel, selenium rectifier and roofing industries, due to its excellent properties such as electrical and thermal conductivity, good corrosion resistance, ease of fabrication and installation. The potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paperboard mills, wood pulp production, and the fertilizer industry. Copper(II) is known to be one of the heavy metals most toxic to living organisms and it is one of the more widespread heavy metal contaminants of the environment.

The conventional methods for removing copper(II) from aqueous solutions include precipitation, oxidation/ reduction, electrochemical treatments, evaporative recovery, coagulation/flocculation, filtration methods, ion-exchange and membrane technologies. These processes may have different limitations: high cost, process complexity and sludge formation, or may be ineffective, especially when the metals in solution are in range of 1-100 mg dm^{-3}. Biosorption processes are being employed as an attractive alternativetechnique for the decontamination of industrial effluents and for the recovery of the retained metals. The major advantages of biosorption over conventional methods include low cost, high efficiency, minimization of chemical or biological sludge and possibility of biosorbent regeneration. A low cost sorbent is defined as one which is abundant in nature, or is a by-product or waste material from another industry.

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Lagenaria vulgaris biosorbent is mostly composed of cellulose and lignin. These components contain many hydroxyl, carboxyl and carbonyl functional groups. Biosorption takes place in heterogeneous system, which involves solid biosorbent and liquid phase (solution) with dissolved species. The mechanism of biosorption is rather complex and involves many different processes: chemisorption, complexation, ion-exchange, chelation, and physical adsorption, which are dependent on the diffusion process.

Fruit of the plant *Lagenaria vulgaris*

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Atomic absorptio spectroscopy (AAS)

Atomic absorption spectroscopy (**AAS**) is a spectroanalytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state. Atomic absorption spectrometry has many uses in different areas of chemistry such as clinical analysis of metals in biological fluids and tissues such as whole blood, plasma, urine, saliva, brain tissue, liver, hair, muscle tissue, semen, in some pharmaceutical manufacturing processes, minute quantities of a catalyst that remain in the final drug product, and analyzing water for its metal content.

The technique makes use of absorption spectroscopy to assess the concentration of an analyte in a sample. It requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and relies therefore on the Beer-Lambert Law.

In short, the electrons of the atoms in the atomizer can be promoted to higher orbitals (excited state) for a short period of time (nanoseconds) by absorbing a defined quantity of energy (radiation of a given wavelength). This amount of energy, i.e., wavelength, is specific to a particular electron transition in a particular element. In general, each wavelength corresponds to only one element, and the width of an absorption line is only of the order of a few picometers (pm), which gives the technique its elemental selectivity. The radiation flux without a sample and with a sample in the atomizer is measured using a detector, and the ratio between the two values (the absorbance) is converted to analyte concentration or mass using the Beer-Lambert Law.

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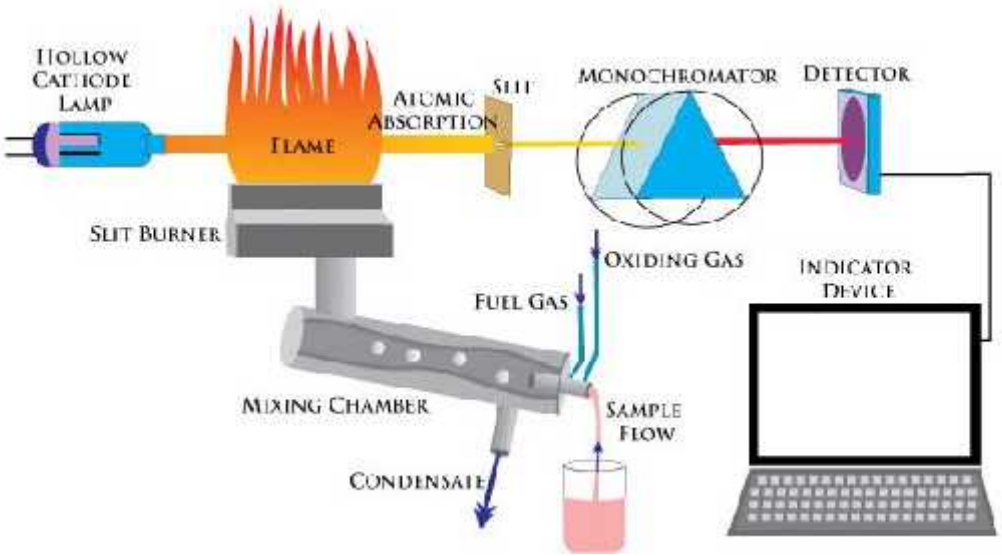
In order to analyze a sample for its atomic constituents, it has to be atomized. The atomizers most commonly used nowadays are flames and electrothermal (graphite tube) atomizers. The atoms should then be irradiated by optical radiation, and the radiation source could be an element-specific line radiation source or a continuum radiation source. The radiation then passes through a monochromator in order to separate the element-specific radiation from any other radiation emitted by the radiation source, which is finally measured by a detector.



A shematic diagram of atomic absorption spectrophotometer

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Material

For this lab exercise, you will need the following material:

Reagents

- nitric acid (HNO_3) obtained from Merck (Germany),
- sodium hydroxide (NaOH) obtained from Merck (Germany),
- Copper(II) nitrate ($Cu(NO_3)_2$) obtained from Merck (Germany).

All chemicals were of analytical reagent grade and were used without further refinement. All solutions were prepared with deionized water. Standard metal stock solution was prepared by dissolving given amounts of analytical grade $Cu(NO_3)_2$. All standard solutions were stored in a refrigerator at +4°C.

Devices

- Atomic Absorption Spectrophotometer;
- pH – meter;
- magnetic stirrer;
- analytical balance.

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Material

For this lab exercise, you will need the following material:

Laboratory equipment

- glasses (100, 250 cm^3);
- volumetric flask 125 cm^3;
- pipette 5 and 20 cm^3;
- graduated cylinder 100 cm^3;
- tubes;
- two funels;
- micropipette 100-1000 ml;
- micropipette 1000-5000 ml;
- filter paper.

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Procedure:

Preparation of biosorbent *Lagenaria vulgaris*

Lagenaria vulgaris is a creeping, hardy plant. It belongs to the Cucurbitaceae family. The outer shell is recognized to be hard and ligneous covering the spongy white pith characterized by bitter taste. The experiments in this study have been carried out using a shell of *L. vulgaris*, grown in the south area of Serbia (near the town of Niš) at about 200 m altitude. Plants were grown under controlled conditions with irrigation and without fertilization, planted at the same time in mid-April and harvested in the mid-October, also all at the same time. *L. vulgaris* shell was roughly crushed, washed with deionized water and grounded by laboratory mill. Biomass was soaked in 0.3 M HNO_3 for 24 h to remove metals bio-accumulated in the plant during growing. After that, biomass was washed with deionized water to remove excess acid and treated with 0.1 M NaOH in period of 30 min. Excess alkali was removed by thoroughly washing and sorbent was dried in the oven at 55±5°C to constant weight. Dried biomass was fractionized using standard sieves (Endecotts, England). The prepared adsorbent was abbreviated as basic *L. vulgaris* biosorbent (LVB) hereafter for convenience.

Basic *L. vulgaris* biosorbent (LVB)

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Procedure:

Batch biosorption experiments

Standard metal stock solution of 1.00 g dm^{-3} Cu(II) was prepared by dissolving given amounts of analytical grade $Cu(NO_3)_2$. Working solutions were prepared just before use by appropriate dilution of the stock solutions. Studies on the adsorption of metal ions by LVB were carried out in batch conditions, by agitating 250 cm^3 of 50.0 mg dm^{-3} metal ion solutions of Cu(II), contacted with 1.00 g biosorbent. The pH of each solution was adjusted to the required value with 0.1/0.01 mol dm^{-3} $NaOH/HNO_3$ solutions using a pH-meter (SensIon5, HACH, USA). The pH was maintained during treatment and kept to within ± 0.2 units by adding 0.01 or 0.1 mol dm^{-3} HNO_3 in small portions. At required time intervals, 4.0 cm^3 of samples were withdrawn and analyzed using a flame atomic adsorption spectrometer AAnalyst 300 (Perkin Elmer, USA).

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DESCRIPTION OF REMOTE ACCESS	
1. NETCHEM COMMUNICATION SIDES (NOTE: NETCHEM Communication is defined as event that involves all kinds of internet interactions (in real time and not in real time) between participants via devices (PCs, laptops, tablets andmobilephones))	
host side (NOTE: Host side of NETCHEM Communication is defined as PC who invites other users to join the session)	**participant's PC in classroom**
guest side (NOTE: Guest side of NETCHEM Communication is defined as PC who joins the invitation to session)	**participant's PC in laboratory**
2. COMMUNICATION SOFWARE	
Team Viewer	Meeting: No
	Remote control: No
	Meeting and Remote control simultaneously: No
Skype	Call 1:1: No
	Conference Call: Yes
3. COMUNICATION HARDWARE	
on host side	**1 PC for each participant**
on guest side	**1 PC, 1 headsets with microphone, camera**
4. INFORMATION EXCHANGE TYPE	
Educational (one side is dominantly receptive)	**Yes**
	Place of Educator participant: guest side
	Number of educator(s): 1
	Place of student participant: **host side**
	Number of student participant(s): **15**
Consultative (two sides are equal in giving-receiving information)	
	Number of host side participant(s): **No**
	Number of guest side participant(s): **No**

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Remote Access Connection Instructions

What makes these labs different and unique from other classroom experiments is that we have incorporated a section in each activity to remotely characterize your samples from your classroom.

Request a remote lab session specifying information such as: the day, the time, and the instrument you are interested in using by visiting our web site:

http://netchem.ac.rs/remote-access

You will see the list of partners with the instruments provided to chose from.

You will be contacted by a Remote Access staff member to set up a test run to ensure you are set up properly and have the required infrastructure.

Send samples or verify the in-house sample you would like us to prepare and load for characterization.

Send your samples to the Remote Access center that you chose on your request.

There are two communications soft-ware packages, that will allow us to communicate instructions and answer questions during the session.

- TeamViewer: You can obtain a free download at:
  https://www.teamviewer.com/en/index.aspx
- Skype

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Remote Access Connection Instructions

You will need:

a) Computer with administrator access to install plug-ins and software

b) An internet connection

c) Speakers

d) Microphone

e) Projector connected to the same computer

f) Web browser (Firefox preferred)

During the test run you can refer to this guide to perform the following steps, but it's very important that you only proceed with these steps during your scheduled times. You may interfere with other remote sessions and potentially damage equipment if you log in at other times.

a) Open and logon to your Zoom/Team-viewer account. You will be given the access code to enter at the time of your test and then again during the remote session.

- If you are using the Zoom software, Remote Access staff will give you the access code.
- If you are using the Team-viewer software, Remote Access staff will give you the ID & password.

b) You should soon see the Remote Access desktop and at this point you can interact with the icons on the screen as if it were your desktop.

c) Switch to full screen mode by selecting the maximize screen option in the top right corner of the screen.

d) Upon completion of the session, move your mouse to the top right corner of the screen, and click on the X to disconnect the remote session. It will ask if you want to end the remote session. Click Yes.

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Author, Editor and Referee References

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Contributors to this material were: Miljana Radovic

Refereeing of this material was done by: _____

Editing into NETCHEM Format and onto NETCHEM platform was completed by: _____

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References and Supplemental Material

The NETCHEM platform was established at the University of Nis in 2016-2019 through the Erasmus Programme.

Please contact a NETCHEM representatives at your institution or visit our website for an expanded contact list.

The work included had been led by the NETCHEM staff at your institution.

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