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Salicylic Acid and 4-Nitroaniline Removal from Water Using Magnetic Biochar: An Environmental and Analytical Experiment for the Undergraduate Laboratory

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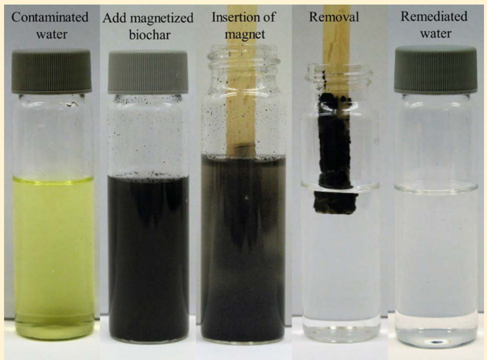
S *Supporting Information*

ABSTRACT: Adsorption studies of salicylic acid (SA) and 4-nitroaniline (4NA) from aqueous solutions were performed with magnetic biochar (MBC) in order to train students in analytical techniques such as standard calibration curves, UV−vis spectrophotometry, and chemical separations within the context of wastewater purification. Analysis of samples purified by MBC enhances student understanding of water quality and the importance of potable water production, a growing worldwide concern. MBC was prepared by iron oxide precipitation onto the biochar surface using an aqueous Fe^{3+}/Fe^{2+} solution followed by NaOH treatment. MBC effectiveness in removing organic contaminants from water was evaluated using UV−vis spectroscopy, Beer's law, and a comparison to standard calibration curves while determining the concentrations of two contaminant compounds. The use of MBC to remove organic contaminants in water highlights the effectiveness of this technique for wastewater remediation and prompt discussion of water quality concerns with undergraduate students.



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Wastewater pollution by organic contaminants is an emerging concern because of potential health impacts.[1] Removing these contaminants from aqueous solution to improve water quality and make water potable has become an increasing focus in both the chemical industry and in academic research. According to the GRACE Communications Foundation, the United States relies on public water systems to treat and deliver over 44 billion gallons of clean water each day.[1] Even with wastewater systems able to deliver large quantities of clean, recycled water, it is estimated that, by the year 2025, 1.8 billion people will live in regions plagued by water scarcity and two-thirds of the world's population will live in water-stressed regions.[2]

Undergraduate student exposure to water quality issues and methods of contaminant removal enhances understanding of important environmental issues. Laboratory activities that concentrate on water treatment and purity typically emphasize filtration techniques and the measurement of pH or water hardness[3−5] with many of the experiments focused toward K-12 students.[6−8] The use of more advanced water quality analyses in the upper-division laboratory has been lacking and needs to be addressed in chemistry curricula to reflect current environmental concerns. This green experiment for the upper-division undergraduate laboratory has been designed using a low cost, sustainable biochar adsorbent for the removal of organic pollutants at the parts per million level. Salicylic acid (SA) and 4-nitroaniline (4NA) are used as two example organic pollutants. Analysis of the removal efficiency of magnetized biochar (MBC) using UV−vis spectroscopy and Beer's law exposes students to analytical instruments and theory within the context of water quality.

Salicylic acid was chosen for this experiment as aspirin is a widely used over-the-counter drug and its metabolites can contaminate the environment. Deacetylation of acetylsalicylic acid (aspirin) produces salicylic acid as an active metabolite often found in industrial effluent at levels up to 54 μg/L.[1] 4-Nitroaniline is a synthetic precursor to pharmaceuticals, dyes, and pesticides and is a common wastewater contaminant.[9] In high concentrations, these potential contaminants can have detrimental environmental effects as 4NA is implicated as a carcinogen while SA can have xenoestrogenic effects. Organic

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contaminants such as these must be removed before treated wastewater is returned to the environment.

Municipal wastewater treatments for pharmaceutical products can be expensive. Current municipal techniques to remove pharmaceutical contaminants in water and wastewater are coagulation and flocculation, membrane purification, advanced oxidation processes, biological treatments, ion-exchange, adsorption technologies, and magnetic separation.[10] Activated carbon is the main material used in adsorption; however, this experiment uses MBC as it offers significant advantages in cost and ease of removal.

Biochar is a low cost adsorbent that can be used for water and wastewater purification. It is produced from biomass, such as wood, leaves, or manure, when it is heated in a container with little or no available air. Thermal processing of biomass, including gasification and pyrolysis, produces biochar as a secondary material.[11] Biochar contains hydroxyl, carboxylic acid, ketone, and ether functional groups on its surface.

Several mechanisms can take place on the biochar surface including electrostatic-repulsion interactions, hydrogen bonding, donor−acceptor complex formation, oligomerization of phenols, and others with many of these mechanisms being pH dependent. The total surface area of the biochar also plays a major role in adsorption of contaminants. Following magnetization, the biochar surface area decreases per unit mass.[12,13] This happens because the magnetized biochar has lower percent carbon than the normal biochar and because the iron oxide precipitate can clog existing biochar pores. The biochar materials can be manufactured in any region that produces an abundance of biomass and therefore can be a low-cost, entirely green alternative to more traditional water purification materials. When biochar is magnetized, its separation from an aqueous environment is fast and efficient as the adsorbant and attached organics can be removed via magnet.

In this upper-division undergraduate laboratory, students use a standard calibration curve to quantify both salicylic acid and 4-nitroaniline concentrations via UV−vis spectrophotometry. Different masses of MBC are then added to sample solutions to adsorb salicylic acid and 4-nitroaniline from the aqueous mixture. MBC is removed after mixing via a magnet, and sample absorbance is measured. Calculations utilizing Beer's Law are used to quantify SA and 4NA concentrations in each sample. Students then assess the effectiveness of MBC in contaminant removal.

The experiment introduces new and interesting approaches to water purification as well as deepens the student's understanding of present environmental concerns regarding pharmaceutical contaminants in wastewater. Students learn valuable analytical laboratory skills such as standard calibration curves, utilization of UV−vis spectroscopy, and Beer's law to determine concentration of an unknown. This experiment reinforces green chemical techniques with a focus toward water quality.

■ EXPERIMENTAL OVERVIEW

Preparation of Magnetic Biochar and Standards

MBC is prepared according to the method given by Mohan et al.[12] with slight modifications. Rinsed ultra biochar (supplied by Biochar Supreme Everson WA) is ground and sieved using a 0.1−0.6 mm mesh before magnetization. Full experimental details of biochar preparation are given in the notes for stockroom preparation in the Supporting Information. MBC can be prepared by the instructor before the student experiment, or incorporated into the experiment as a two-week exercise. Once prepared, MBC can be stored in a closed container and used for multiple lab sections. Standard solutions of 25, 20, 15, 10, 5, and 1 ppm are prepared by students using a 25 ppm stock solution that contains both SA and 4NA. Full instructional details for the experiment including safety information is provided in the Supporting Information.

Data Analysis and Results

According to Beer's law, the concentration of contaminants is proportional to the absorbance of the sample. Figure 1 shows

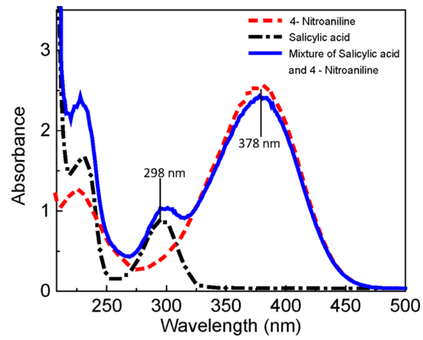

Figure 1. UV−vis spectrum of 4-nitroaniline (25 ppm), salicylic acid (25 ppm), and mixture of salicylic acid + 4-nitroaniline (25 ppm) in distilled water.

the UV−vis spectra from 200 to 500 nm for the two analytes. Salicylic acid and 4-nitroaniline show maximum absorbances at 298 and 378 nm, respectively, and can be combined into a single stock solution. The combined sample introduced error into the UV−vis absorbance, but we found students were able to accurately determine concentrations of both analytes with less than 7% error.

The absorbance of each of the 6 standard solutions is measured and plotted versus their concentration, resulting in two linear calibration curves (Figure 2). Varying masses of

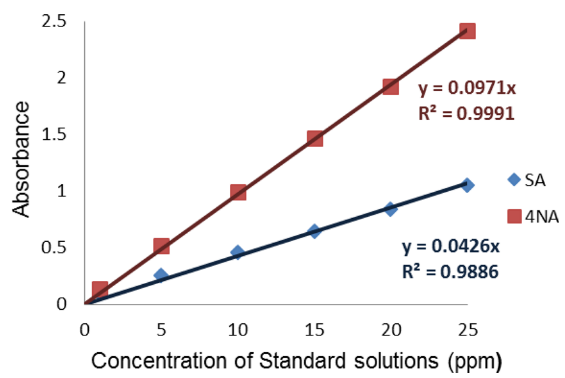

Figure 2. Linear calibration curves of the 6 standard solutions.

MBC are then added to 6 glass vials containing 25 mL of the standard SA + 4NA (25 ppm) solution and vortexed for 2 min to allow organic compound−MBC interaction. A magnet is then inserted into each solution to remove all the MBC and the attached analytes. Figure 3a shows the vials after MBC clearance using the magnet. Absorbance of each purified solution is measured (Figure 3b) and the concentration of each

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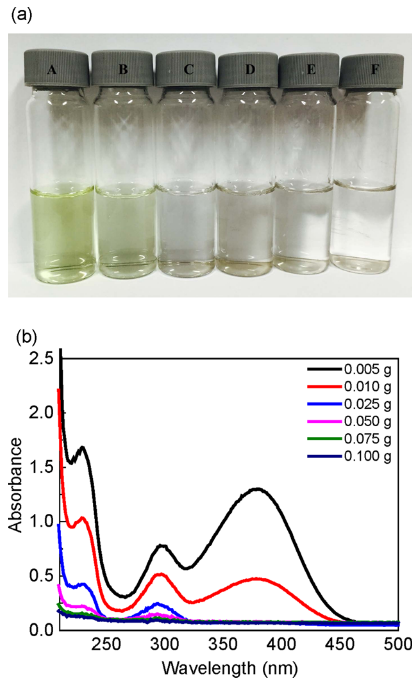

Figure 3. (a) Solutions showing adsorption of SA and 4NA (25 ppm each) using different masses of MBC (A) 0.005, (B) 0.010, (C) 0.025, (D) 0.050, (E) 0.075, and (F) 0.100 g. (b) UV−vis spectrum of resulting solutions.

analyte determined using the equation generated by the calibration curve.

The percentage analyte removed by MBC from each sample is determined using the following equation

$$\% \text{ removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

Typical results are shown in Figure 4.

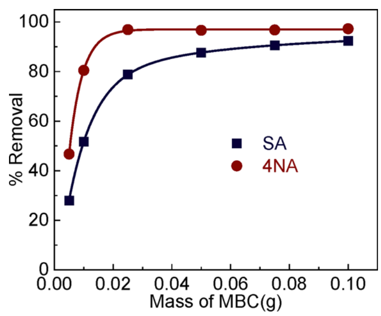

Figure 4. Percent removal vs mass of MBC for SA and 4NA.

Also, the amount of analyte removed per gram of MBC (adsorption efficiency; q_e) is calculated using

$$q_e = \frac{V(C_0 - C_e)}{M} \quad (2)$$

where the following abbreviations apply: C_o is the initial analyte concentration (mg/L), C_e is the equilibrium analyte concentration (mg/L), V is the solution volume (L), M is the mass of MBC added (g), and q_e is the adsorption efficiency adsorbate/adsorbent (mg/g)

The adsorption efficiency using 0.05 g of MBC was determined by students on average to be 10.98 mg/g MBC for SA and 12.46 mg/g MBC for 4NA. Students use the calculated adsorption efficiency to identify ideal MBC ratios for wastewater remediation.

■ HAZARDS

Students should wear goggles and gloves throughout the experiment and prevent skin contact with all chemicals. All of the liquid chemical waste must be disposed in a hazardous waste container labeled as hazardous aqueous waste. Solid waste (MBC) must be disposed in a waste container labeled as solid waste or regenerated according to provided instructions.

■ STUDENT LEARNING OBJECTIVES AND OUTCOMES

This upper-division undergraduate experiment was performed with two different groups of upper-division analytical undergraduate students (20 students in total) in an instrumentation analysis course and also performed with middle- and high-school teachers (31 teachers total) during two summer training workshops. The learning objectives for this experiment are 2-fold: (1) introduce Beer's law and the use of UV−vis spectroscopy to analytical students and (2) introduce the context of water purification and water quality concerns to undergraduates. The 20 students exposed to this undergraduate experiment were concurrently registered in an analytical chemistry lecture course. Of those tested, students performing this experiment scored a grade of 70th percentile or better on exam questions related to UV−vis spectroscopy (86%) and Beer's Law (92%).

Water purification and water quality were not tested in the analytical course, but student interest in these issues has increased after the experiment was introduced in analytical lab. MSU students involved with this experiment have subsequently enrolled in an upper-division Environmental Chemistry course, founded a Soil and Water Conservation Society on campus, and formed a group to compete in the Campus Water Matters Challenge hosted by the South Eastern Conference. The student leaders at MSU have chosen to promote a biochar solution to aid in the removal of fertilizers from stormwater runoff before the contaminated water can reach our natural waterways. This is a direct expansion of the experiment described in this paper.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00154.

Student laboratory experiment, instructor answer key, instructor's notes, and notes for stockroom preparation (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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