EXPERIMENTS AND OTHER LEARNING ACTIVITIES USING NATURAL DYE MATERIALS

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Ever-increasing concerns and constraints regarding student safety and health, waste disposal, and liability can significantly hamper development of interesting and relevant laboratory experiences in a chemical engineering program. Using chemical reagents is likely the most problematic of the possible safety and health concerns faced by chemical educators. While placing the highest priority on the safety of our students, we still wish to provide learning experiences that prepare them for their careers, meet our learning objectives, and are (we hope) inherently interesting. Approaches that can be taken to provide especially safe laboratory experiences are many; some of them include

- *Avoiding chemical reagents (other than water and air) altogether*
- *Using microquantities of chemical reagents*
- *Investing in ultrasafe equipment, facilities, and specialized training*
- *Using simulations and/or remote laboratory experiences*

Each of these approaches has some significant advantages, but each also has its disadvantages: avoiding chemical reagents altogether is impractical when learning objectives involve chemical reaction kinetics, for example, and using only microquantities is impractical when learning objectives involve experience with pilot or industrial-scale unit operations.

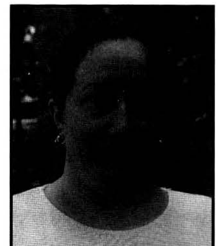
In recent years, an additional personal concern of the author has been that chemical engineering students have little exposure to or opportunity to work with materials in "raw" form. Laboratory materials nearly always comprise highly processed and purified reagents. This, despite the fact that a very large fraction of the top production chemicals produced in the United States[1] are commodities produced from basic raw materials, including petroleum, mined goods, agricultural products, surface and ocean waters, and air.

A description of an experimental approach designed to support a particular chemical engineering technical topic, but that can be adapted to other chemical topics and other uses, is presented in this paper. The hope is that it can serve as a guide to others contemplating incorporating raw and natural materials into chemical engineering laboratory experiences.

MOTIVATION

In addition to the learning goals common to any laboratory experiment in any chemical engineering laboratory course, an additional cognitive[2] learning goal desired by the author was that students achieve knowledge of some differences between raw and highly processed materials when incorporated into a chemical process. Some additional elements motivating the use of natural dyestuffs include

- Safety Natural dyestuffs have been in use for many centuries; many of them are extremely well characterized, and the ones we chose have no safety warnings associated with them. We insist on the best laboratory and safety practice at all times, but the safety of these materials was a valuable aspect of their performance.
- Environmental Friendliness As a result of their low hazard, disposal of wastes generated when using



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natural dyestuffs is simple—dye extracts pose no problems to municipal water treatment systems, and spent dyestuffs can be disposed of in general waste. (The author prefers to collect the dyestuffs for garden composting.)

- Cost Commercially available dyestuffs range in price from very expensive (indigo and carmine, up to $50/lb) to modest (logwood, $8/lb), while some usable materials are nearly free (onion skins).
- Aesthetics Natural dyestuffs and their extracts are low-odor and generally pleasant-smelling, and the colors of the extracts can be quite vivid, which is of additional appeal to students.
- Topical Richness and Complexity Students often become bored when working with materials and processes that are extremely well-characterized—"Why should I bother studying this when I know the answer already?" is a common complaint. Although there is a very large amount of information available on the production of natural dyes, it is mostly in the form of recipes and "folk wisdom." This makes an engineering approach to their processing both interesting and useful. I have had more than a few students speculate that application of chemical engineering principles could possibly lead to profitable commercial production of natural dyes.

NATURAL DYESTUFFS

Forty-seven plants are listed in *Dye Plants and Dyeing.*[3] A selection of plants for each major color group is given in Table 1. In addition to plant sources, there are some animal sources (cochineal, for example, is extracted from the carapaces of scale insects that live on cactus plants) and mineral sources (for example, ochre, from a type of iron ore). A variety of sources for some of the more readily available dyestuffs can be found with minimal search on the World Wide Web. Prices for logwood chips, a moderately expensive material, are about $30 per pound retail; fifty grams of chips is enough for 15 or more small-volume (50 ml or less) experimental extractions. Less expensive dyestuffs include alkanet root (about $4 per pound), madder root (about $4-$10 per pound), and osage orange sawdust (about $10 per pound). In addition to a wealth of material available through the World Wide Web, there are many text references available detailing dye plants,[3] dyeing recipes and approaches,[4,5] and world dyestuff production.[6]

Experiment for Using Statistical Design of Experiments to Screen Processing Factors

This laboratory experiment is conducted in the junior-level chemical engineering laboratory course at Arizona State University. The course is designed to meet six learning objectives:

1. *Students will be able to design experimental runs to achieve a specified experimental goal and perform the experiments in a safe, ethical, and professional manner.*
2. *Students will be able to record and analyze experimental data, and to interpret analyzed results using appropriate theory and models.*
3. *Students will be able to effectively communicate all aspects of their experimental work and analyses in oral and written form.*
4. *Students will be able to make appropriate use of a computer in data analysis and in oral and written communication of their experimental work.*
5. *Students will be able to perform technical work in teams.*
6. *Students will have demonstrated the above skills in the context of chemical engineering knowledge acquired in earlier courses.*

The natural dye extraction experiment is implemented to introduce students to statistical design of experiments (DoE). The experiment is framed in the context of performing DoE on a variety of processing factors for dye extraction as if for eventual development of a full commercial process.

Students are provided with the following context statement

TABLE 1
Some Plant Sources of Natural Dyes for Various Colors[3-5]

Yellows	Blues	Reds	Greens	Purples	Oranges	Browns	Greys/Blacks
Black Oak Bark	Logwood	Madder	Ivy Berries	Logwood	Annatto	Cutch	Black Walnut
Fustic	Indigo	Brazilwood	Wallflower	Blackberry	Coreopsis	Black Walnut Hulls	Logwood
Osage Orange	Woad	Bloodroot	Lily of the Valley	Alkanet	Silver Birch	Elderberry	Mountain Laurel
Turmeric	Red Cabbage	Munjeet	Plantain Roots	Grapes	Turmeric	Henna	Sumac
Saffron		Pokeweed	Nettle	Red Cedar Root		Onion	Iris Root
Weld		Strawberries				Yew	
		Cherries				Sumac Leaves	
		Raspberries				Juniper Berries	
		Beets				Coffee Grounds	

and experiment-specific learning objectives:

"Natural" or naturally based consumer products currently have a limited, but growing (and devoted!), customer base. This is especially true for clothing and in cosmetics and personal care products, where "organically grown" fibers or a "naturally derived" specialty chemical (to be used in a cosmetic, a shampoo, fragrance, or nutraceutical), having the same functionality and performance as a "non-natural" fiber or chemical might sell for ten-or-more times the price.

A challenge in using "natural" feedstocks in chemical processes is that they have properties that can be quite variable—consider, for example, indigo (the leaves, stems, and flowers of which contain the familiar blue dye of blue jeans). The ***productivity*** *(bushels of plant matter/acre) of land planted in indigo will depend on all the usual agricultural factors (climate factors, water factors, soil-type factors, farming-practice factors). The* ***quality of the plants*** *themselves will also depend on most of these agricultural factors —the 'quality' including concentration of the dye chemicals of interest, their ease of processing, and the types and kinds of impurities. The* ***quality and quantity of extracted dye*** *will depend on the plant quality as well as on a host of processing factors—extraction pH, oxygen concentration in extraction bath, extraction time, temperature, degree and types of mixing, extraction co-solvents, etc.*

For this experiment, you will be assigned a particular dyestuff (brazilwood, logwood, or madder) and perform a statistically designed ("DoE") experiment with the intent of testing possible dye processing factors for significance. You should perform this experiment in the context of the development of a commercially viable process for extracting natural dyes, with a view to tapping into the growing market for 'natural' materials. You will generate an appropriate statistical hypothesis, design the experiments required to test the hypothesis, conduct the experiments, analyze the results, and either falsify or support the proposed hypothesis.

The learning objectives for this experiment are that you

1. Achieve and demonstrate Comprehension Level of Learning for generation and testing of DoE screening-type hypotheses.

2. Achieve and demonstrate Application (Analysis) Level of Learning for planning experiments, in particular, full-factorial DoE screening experiments.

3. Achieve and demonstrate Application (Analysis) Level of Learning when applying principles from earlier ChE and core courses to analysis of experimental data.

Pre-Lab Expectations • Students are assigned a particular dyestuff (brazilwood, logwood, or madder) and are required to do some background research on natural dyes in general and on their assigned dyestuff in particular. From this background research they generate a set of possible "measures of goodness" or outcomes that can be used to characterize their experimental outcome. From this set, they choose one (normally, dye concentration or strength). They also generate a large set of possible processing factors influencing the output variable. They narrow these down to four to be tested in a full-factorial two-level screening type experiment and develop the details of the experimental runs in consultation with the instructor (issues: safety, practicality, available processing, analytical equipment, etc.). After being signed off by the instructor, they conduct the experiment.

Conduct of the Experiment • Supplies must be provided to allow students to test processing factors:

- *Temperature: hot plates and/or temperature baths, temperature measurement*
- *Extraction time: timers*
- *Agitation: Stirrers, shakers, or agitators*
- *Solvent composition: reagents and chemicals, balances and/or graduated cylinders, pipettes, etc.*
- *Pre-extraction dyestuff soaking: reagents, timers, etc.*
- *Dyestuff particle size: mortar and pestle, grinder, size screens, etc.*

It is important to either provide students with a comprehensive list of available equipment and supplies in the laboratory or require them to specify required supplies at a pre-

TABLE 2
Typical Student Choices for High and Low Factor Levels for Statistical DoE Experiment

Process Factor	*Temperature*	*Solvent*[a]	*Pre-soak*	*Extraction time*	*Agitation*	*Dyestuff particle size*[b]
Typical 'high' factor value	100°C	ethanol	24 hours 20°C	20-50 minutes	high speed	as received
Typical 'low' factor value	20°C	water	none	1-5 minutes	none	reduced

[a] Students were permitted to choose water, ethanol, or with justification from the literature, to choose other "safe" solvents or solvent systems (e.g., aqueous acetic acid, saline solution)
[b] As-received particle size varied significantly for different dyestuffs: madder was received as roots with an average root piece of 4x40 mm, while brazilwood was received as roughly 300 μm particles. Reduction was accomplished via laboratory blender or by mortar and pestle.

lab meeting to assure that necessary supplies are adequate for the testing of their chosen factors. Table 2 gives typical low and high values chosen by students in the conduct of their DoE experiments.

Dyebath Analysis • There are several approaches that can be taken to analyze dye concentration—a colorimetric approach, where samples of extract from each run are compared to a wide set of known standards; a spectroscopic approach where samples of extract from each run are analyzed using UV-vis spectroscopy and Beer's law; or an analytical chemistry approach where extracts are further treated to purify (and weigh) the pure dye. In both colorimetric and spectroscopic approaches, a significant challenge is that the range of dye concentrations in the extracts might span three or even four orders of magnitude. In this case, neither the eye nor the spectrometer will have enough dynamic range to fully accommodate all samples, so a stronger sample might have to be pre-diluted to fit into a narrower 'instrumental' range.

Data Analysis • The experimental data set will comprise a matrix of data that is analyzed using DoE algorithms, normally via computer programs such as Minitab, JMP, Design-Expert, Fusion Pro, or add-on statistical software for MS-Excel such as XLSTAT.[7] Depending upon the students' statistics background, required analysis can be as simple as a significance test for each of the factors, or as complex as response surface analysis. In this course, students were only required to complete a significance test.

LEARNING EFFECTIVENESS

Students tended to rather easily develop a competent DoE experimental design, but they often exhibited confusion between experimental design in the statistical sense and experimental planning—they often did not adequately imagine the actions they would be taking in the laboratory, and as a result they underestimated the time required or did not adequately

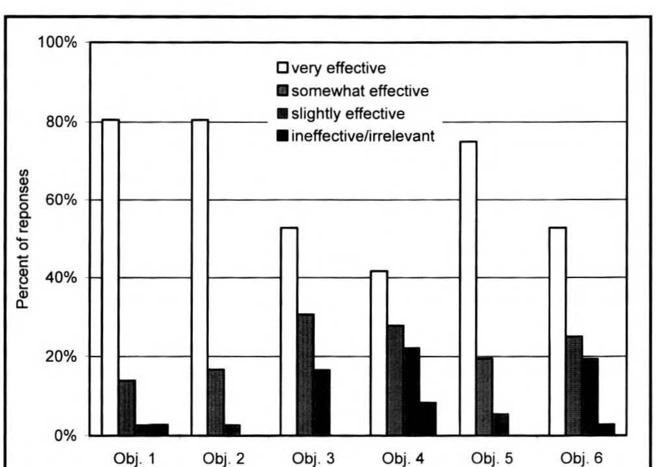

Figure 1. *Student ratings of the effectiveness of the dye-extraction experiment in meeting each of the course learning objectives (listed in the text).*

plan for the complexity of simultaneous runs. In this implementation, we used colorimetric analysis of dyebaths to ascertain extraction effectiveness. We plan on implementing spectrophotometric analysis in the next implementation, both as additional training for students in modern experimental methods and to enhance the precision of the experimental results.

Students were asked to rate the effectiveness of the dye extraction experiment and report-writing experience on their achievement of each of the course's learning objectives. Results are shown in Figure 1 for the Spring 2003 semester, the first implementation of this experiment.

On average, students rated the dye extraction experiment as a very effective activity toward the achievement of three of the course learning objectives (ability to design and perform experiments, ability to record and analyze data, and working in teams), somewhat-to-very effective for two objectives (ability to communicate effectively and apply skills in a chemical engineering context), and somewhat effective for one (ability to effectively use computers). These data indicate that the students viewed the learning experience as integrative within the course, which was certainly the intention of the instructor.

Positive comments about this experience included

- *I think the lab was the most important assignment of the course because it encompasses all of the learning objectives and seemed to be the climax of the course...I think more emphasis should be placed on it.*
- *Out of the tasks completed in this course, the design of experiments was the most useful in achieving the course learning objectives.*

Student suggestions for how to improve the experience mostly referred to a wish for more training in appropriate software for statistical analysis of their results. For example,

- *...require students to have more computer interaction*
- *...have an in-class tutorial on how to use available software*

MASS TRANSFER EXPERIMENTS

These are described for sophomore- or junior-level work after students have been introduced to simple mass transfer concepts. Simple estimation of an overall mass transfer coefficient can be obtained by looking at the driving force for extraction. If C represents the concentration of the dye in the extract, and C_{eq} represents the equilibrium (or saturation) concentration of dye in the solvent, then assuming that the mass transfer coefficient is dominated by resistance at the dyestuff/solvent interface, the relation

$$\frac{\partial C}{\partial t} = k\left(C_{eq} - C\right) \qquad (1)$$

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lems more realistic. In addition, the RTD can be applied to other models, including a one-parameter dispersion model, to characterize nonideal reactors. The validity of model assumptions must be checked before applying any model, however.

The nonideal reactor analysis using CFX was implemented in the junior-level chemical reaction engineering course in the spring of 2002. Student feedback led to the importance of considering some issues when implementing CFD into the curriculum. First, since students were only exposed to CFX the prior semester, assigning the project for a group, rather than an individual, enabled students to spend more time on the analysis. Second, students were often frustrated when drawing the geometry in CFX. Perhaps an instructor should consider developing a geometry database so students can spend more time analyzing reactor geometries and understanding nonideal concepts rather than drawing the geometries. In conclusion, the use of CFD programs such as CFX will enable students to be more prepared to enter today's workforce and to solve the difficult problems that arise with nonideal reactors.

REFERENCES

1. Levenspiel, O., *Chemical Reaction Engineering,* 3rd ed., Wiley, New York, NY (1999)
2. Fogler, H.S., *Elements of Chemical Reaction Engineering,* 3rd ed., Prentice Hall, Upper Saddle River, NJ (1999)
3. Davis, R.A., "Nonideal Reactors in Process Simulators," *Proc. AIChE Conf.,* Los Angeles, CA, p. 166, (2000)
4. Dutta, S., and R. Gualy, "Build Robust Reactor Models," *Chem. Eng. Prog.,* p. 37, October (2000)
5. Bakker, A., A.H. Haidari, and E.M. Marshall, "Design Reactors via CFD," *Chem. Eng. Prog.,* p. 30, December (2001) ❒

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is a reasonable starting approximation. After experimental determination of C_{eq} (either from the asymptote of the concentration/time results or from a separate experiment), concentration vs. time data at constant processing conditions (temperature, stirring, dyestuff particle size, etc.) can be analyzed graphically or analytically to determine the mass transfer coefficient from the time dependence of the concentration

$$C_{eq} - C = kC_{eq} \exp(-kt) \qquad (2)$$

Further experiments can be designed to readily examine the effects of solvent, temperature, stirring, dyestuff particle size, and soaking on C_{eq} and on k.

ADDITIONAL OPPORTUNITIES

Aspects of this approach that were listed at the start of this article suggest some further opportunities in using natural dyestuffs:

• ***Other ChE Experiments***

This paper describes implementation for supporting the learning of statistical design of experiments relevant to early-stage process development. Variations of this experiment could support other ChE topic areas and concepts, including thermodynamics (dye solubility with temperature, solvent), unit operations (post-extraction filtration, operation costs as a function of dyebath concentration and production rate, countercurrent stage-wise extraction), and reaction engineering (for dyestuffs requiring some chemical reaction as part of the processing, such as indigo).

• ***Distance Experiment***

A kit for the conduct of this experiment or something like it could be generated for a true distance experiment; the safety of the materials makes it possible to perform an aqueous extraction experiment in a home kitchen—analysis could be performed by color comparison to a printed standard sheet.

• ***Hands-On Recruiting Activity/Contest***

Students could be challenged to most-closely match a target color using the smallest amounts of materials. They could be supplied with samples of a variety of dyestuffs, water, vinegar, baking soda, and perhaps some nontoxic metal salts. Materials could be price-labeled and students required to complete their work within a budget.

SUMMARY

The main purpose of this article is to spark interest in the use of natural raw materials in a variety of chemical engineering educational contexts, especially laboratory experiences. We have found that students respond positively to the laboratory use of these materials in the form of natural dyestuffs. Such materials can provide safe, environmentally friendly, aesthetically engaging hands-on experiences to support a variety of learning goals in the chemical engineering context.

REFERENCES

1. "Facts and Figures for the Chemical Industry," *Chemical and Engineering News,* 42 (2002)
2. Bloom, Benjamin S., Ed., *Taxonomy of Educational Objectives: Book 1, Cognitive Domain,* Longman, New York, NY (1984)
3. Cannon, John, and Margaret Cannon, *Dye Plants and Dyeing,* Herbert Press, Kew, England (1994)
4. Liles, J.N., *The Art and Craft of Natural Dyeing*, University of Tennessee Press, Knoxville, TN (1990)
5. "Making Natural Dyes from Plants," pioneerthinking.com at <http://pioneerthinking.com/naturaldyes.html> (2003)
6. Green C.L., *Natural Colorants and Dyestuffs: A Review of Production, Markets, and Development Potential,* Food and Agriculture Organization of the United Nations, Rome, Italy (1995)
7. Software sources: Minitab from Minitab Inc., State College, PA; JMP from SAS Institute, Inc., Cary, NC; Design-Expert from Stat-Ease, Inc., Minneapolis, MN; Fusion Pro from S-Matrix, Inc., Vancouver, BC; SC-State from Addinsoft, Brooklyn NY ❒