A Simple Flotation De-inking Experiment for the Recycling of Paper

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Abstract

Flotation de-inking technology is used in the paper recycling process to preferentially remove hydrophobic contaminants such as inks and toners from a slurry of fibers in water. In the process, fine air bubbles are introduced into the suspension and the hydrophobic contaminants preferentially attach to the bubble-water interfaces, are carried to the top of the flotation vessel and are skimmed away in a reject stream. Clean fibers are taken from another port of the vessel as the accept stream. This communication describes a simple, inexpensive method to execute in the laboratory a batch type flotation de-inking process on wastepaper. In the experiment, wastepaper is dispersed in water and then de-inked using a laboratory flotation apparatus readily assembled from common lab equipment. The product streams are collected on filter paper to determine the contaminant removal efficiency and the fiber yield. The experiment is useful for middle/high school science courses or introductory level college environmental, chemical engineering, or chemistry courses in need of a simple experiment that demonstrates, for example, concepts in separation technology, surface science, or mass balances. A host of complementary information pertaining to the manufacturing and recycling of paper and many other paper making and paper recycling activities can be found at the following website: http://www.cfr.ncsu.edu/wps/k12activities/lectures.htm.

Keywords

Paper recycling, wastepaper, de-inking, flotation, contaminants, air bubbles, yield, removal efficiency, lab experiment, chemical engineering, demonstrations, environmental/green chemistry, laboratory instruction, separation science, and surface science.

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Lab Summary

Flotation de-inking is used in paper recycling processes to preferentially remove hydrophobic contaminants such as inks and toners from a slurry of fibers in an aqueous phase. In the process, fine air bubbles are introduced into the suspension and the hydrophobic contaminants preferentially attach to the bubble-water interfaces and float to the surface. The foam on the top of the surface laden with contaminant is skimmed away resulting in the separation.

This paper describes a laboratory exercise for the flotation de-inking of wastepaper. The exercise consists of disintegrating printed wastepaper in a blender and then removing the ink or toner contaminants by pumping air bubbles through the suspension using an aquarium pump (**Figure 1**) or other source of air bubbles. Foam is taken off the top of the container that is rich in ink (the reject sample) while the cleaned fiber remains in the container (the accept sample). After the experiment the accept and reject samples are analyzed for ink concentration and for fiber content.

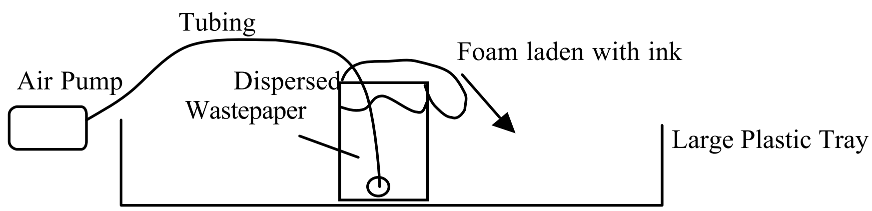

Figure 1. Schematic Drawing of the Laboratory Flotation Experiment.

Common, inexpensive equipment and no chemicals (other than a surfactant to enhance foaming) are needed for the exercise. The experiment is useful for middle/high school science courses or introductory level college environmental, chemical engineering, or chemistry courses in need of a simple experiment that demonstrates, for example, concepts in separation technology, surface science, or mass balances. It can be run as a demonstration, assigned as a lab exercise, or be used as the basis for an independent research project. The experiment has been executed hundreds of times in our department. It has proven to be extremely reliable and consistent in its performance. The removal efficiency of toner and the fiber yield of the process are both usually in the range of 60-80% and vary with the wastepaper disintegration process, the type of paper, the type and amount of foaming agent and the type of toner or ink.

The laboratory demonstrates several phenomena involved in surface science, separation technology, and chemical engineering. One of the strengths of the lab is that it is very visually stimulating; the students can easily observe surface science phenomena at work in an important technological separation process. The recycling aspects of the experiment are important, as students are motivated to learn about recycling and environmentally responsible processes.

This laboratory experiment description is the first known by the author pertaining to flotation de-inking for paper recycling (non-research). Relative to some related laboratory exercises in flotation separations [1-3], the laboratory exercise described herein has several advantages including the use of common inexpensive equipment, simple methods for analysis, and safe and simple procedures. This, combined with the pertinence to recycling and the environmental conservation of resources, makes the experiment an enjoyable, educational hands-on experience.

A host of complementary information pertaining to the manufacturing and recycling of paper and many other paper making and paper recycling activities can be found at the following website: http://www.cfr.ncsu.edu/wps/k12activities/lectures.htm.

Hazards

Care must be taken in operating a blender. Never stick your hand into a blender cup that is installed on the motor. Always blend with the cover on.

Lab Documentation

Importance of Paper Recycling

Currently, over 50 million tons of the approximately 100 million tons of paper consumed in the United States are recycled. Paper is by far the single type of material that dominates municipal solid waste facilities, accounting for about 35% by weight of the waste. The effective recycling of wastepaper is crucial to the future of our society. However, the extent and methods used to recycle waste need to be chosen very carefully. Often, compromises must be made so that recycling processes provide clean, high quality products and also so that the recycling process is efficient in its use of resources such as electricity and water. This experiment demonstrates this concept using the flotation de-inking process for wastepaper.

Introduction to Flotation De-inking

Flotation technology is used in paper recycling processes to preferentially remove hydrophobic contaminants such as inks and toners from a slurry of fibers in water [4-5]. A continuous feed of fiber, contaminant and water enters the flotation cell and is mixed with fine air bubbles. The hydrophobic contaminant particles preferentially attach to the air bubble-water interface and rise to the top of the cell. A layer of contaminant-laden foam (stabilized by a foaming agent added to the feed) is taken off the surface of the cell as the reject stream. The fiber slurry is removed from the tank elsewhere as the accept stream and is disposed. It should be noted that the separation process is never perfect; there is always some contaminant in the accept sample and fiber in the reject sample.

For a flotation separation device both the yield of fibers and the removal efficiency of contaminants is important. The fiber yield describes the fraction of dried solids (in particular fiber in paper recycling) that are accepted from the process divided by the amount of dried solids that are fed to the process and can be calculated as follows:

$$\text{Fiber Yield} = 100\% * \text{ACCEPT Weight} / \text{FEED Weight}$$

The cleanliness efficiency is used as a measure of the percent decrease in contaminant concentration in the ACCEPT sample relative to the FEED sample and can be calculated as the following:

Cleanliness Efficiency = 100% (FEED Count – ACCEPT Count)/FEED Count

In this case, the term count stands for any type of consistent measure of contaminant concentration in each sample. Examples of concentration units are counts of contaminant/square meter or area covered by dirt divided by area of paper. Both the fiber yield and cleanliness efficiency are discussed in more detail later in a Calculations section.

It is generally found that the operating conditions of a separation process must be set as to balance the need for high fiber yield and high cleanliness efficiency. To produce very clean accept sample, generally a large fraction of the feed material must be rejected and the fiber yield is low. By the same principle, by not rejecting a small fraction of the feed material the fiber yield is high but generally the cleanliness efficiency is low. Therefore, depending on the needs of the manufacturing process, a set of conditions that compromise between fiber yield and cleanliness efficiency is used.

Mechanism of Separation in Flotation De-inking

What is the underlying reason that flotation de-inking can effectively separate contaminants from paper fibers? Hydrophobic (meaning water-hating) contaminants preferentially attach to the air bubble-water interface relative to fibers. This is best understood by noting that paper fibers are constituted in a majority by cellulose molecules that contain hydroxyl groups that may favorably interact with the water molecules through hydrogen bonding whereas hydrophobic contaminants do not. It is more energetically desirable for the hydrophobic contaminants to exist at an air-water interface than for the cellulose fibers. Thus, the hydrophobic contaminants will preferentially attach to the air bubble-water interface to minimize the water/contaminant interface. Another way of saying this is that the fibers are “more wettable” by the water phase than the hydrophobic contaminants.

A simple indication of the hydrophobicity of a material can be obtained by determining the contact angle of water on the material surface in air [6]. The contact angle is defined as the angle of contact of a liquid as measured through the liquid (**Figure 2**). Lower contact angles indicate a more hydrophilic (water loving) material. Contact angles greater than 90° are indicative of surfaces that are non-wetting by water. For example, applying a car wax (a hydrophobic coating) to the surface of a car causes the car surface to be not wettable by water. Thus, the "beading" effect of water on the car surface is observed.

The contact angle is useful in understanding how flotation de-inking works. For example, toners often have contact angles (water in air) in the range of 100° and cellulose fibers often have contact angles in the range of 30°. Thus, it is expected that the toner (more hydrophobic) will attach to the air bubble-water interface preferentially resulting in the separation of toners and fiber (i.e., de-inking).

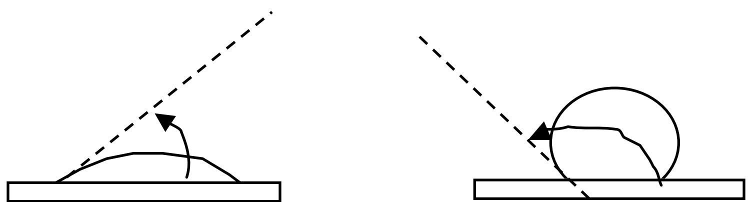

Figure 2. Examples of Water Drops on Hydrophobic and Hydrophilic Surfaces. The contact angle is measured from the surface through the liquid to the tangent of the liquid surface as indicated by the arrows.

Industrial flotation processes have removal efficiencies for most inks and toners that can range from 30 to 95%. The efficiency depends on many variables including the type of wastepaper, type of print, quality of the water, detachment of the ink from the fiber surfaces and the operating conditions of the flotation cell. Often times multiple flotation cells are used in series to improve overall contaminant removal. Flotation de-inking is not useful for removing very small (less than 1 micron) or very large contaminants (greater than 200 microns). Very small particles tend to be swept around air bubbles in the fluid streamlines rather than attaching to the bubble-water interface. Very large particles attach to the bubble-water interface but then detach due to fluid forces pulling the particles off the air bubble.

Overall Paper Recycling/De-inking Systems

The flotation de-inking process is always incorporated into a recycling process that consists of other types of contaminant removal processes. These may include washing (removes small particles), centrifugal cleaning (removes particles based primarily on apparent density and shape), and screening (removes large particles) that remove different types of contaminants with different characteristics [4-5]. In addition to separation processes, many recycling processes also have a bleaching operation in order to bleach dark or dyed fibers that cannot be separated from light fibers. In a successful de-inking process all of these operations are staged in a way to complement each other and produce a robust system able to handle different types and concentrations of contaminants.

Preface to the Experimental Section

The described experiment is a simple way to demonstrate the flotation process. The flotation process is a good example of a separation operation for the recycling of waste paper. The experimental procedure described is a batch simulation of what is typically a continuous process in industrial practice. By following all of the steps, the process can be quantitatively analyzed as described. The steps can be simplified if only a qualitative response is required.

Hazards:

Care must be taken in operating a blender. Never stick your hand into a blender cup that is installed on the motor. Always blend with the cover in place.

Equipment and Materials

1. Common Household Blender or equivalent.

2. 24 quart rectangular plastic tray, about 2 feet by 1 foot by 4 inches. Exact dimensions are not important. Must be able to hold a 1000 mL beaker (see below).

3. Aquarium air pump (example: Whisper 500 by Tetra, Blacksburg VA) with tubing and an air diffusing stone (example: AS2 Air Stone Standard by Tetra, Blacksburg VA) attached to the end of tubing. Alternatively, any pressurized air source connected by tubing to a glass fritted air dispersion tube or disk (example: Pyrex Brand Tubes with Fritted Disk Concentric with Stem, Fisher Cat No. 11-137-5B, Fisher Scientific, Pittsburgh, PA)

4. Toner printed copy paper. Recommended print is 12-point font double-spaced on the entire page. High-speed copiers tend to produce wastepaper that is most easily flotation de-inked whereas slow, personal computer printers produce more difficult to flotation de-ink wastepaper.

5. Foaming Agent. Liquid dishwashing detergent. Examples of commercial detergents that will work are Palmolive, Dawn and Ivory Dish Detergent. The actual foaming agent used in industrial applications is a highly engineered blend of surfactants. *Samples of industrial foaming agent formulations will be provided by the author on request.*

6. A Buchner funnel vacuum filtration apparatus with coarse filter paper and vacuum source. Recommended paper: Whatman Filter Paper 4 Qualitative Circles 150 mm Diameter 1004-150, Fisher Cat. No. 09-825E, Fisher Scientific, Pittsburgh, PA. Recommended Buchner Type Filtering Funnel: Coors Porcelain with Fixed Perforated Plate, Coors No. 60246, Fisher Cat. No. 10-356G, Fisher Scientific, Pittsburgh, PA. Recommended Filter Flask: Pyrex Brand with Tubulation, Corning No. 5340-1L, Fisher Cat. No. 10-180F, Fisher Scientific, Pittsburgh, PA.

7. Constant temperature oven.

8. A gravimetric balance accurate to 0.01 grams minimum.

9. A long (12 inch) stirring rod or spoon.

10. A 2000 mL graduated cylinder

11. A 5 mL pipet

12. Three 1000 mL glass beakers (example: 1000 mL Pyrex Beaker, Fisher Cat. No. 02-540P, Fisher Scientific, Pittsburgh, PA)

Experimental Procedure:

1. Oven dry three filter paper circles by placing them in an oven at 105°C. Drying should be performed for at least 15 minutes. Remove the filter papers from the oven and quickly weigh them and record the weight. The paper will absorb moisture from the air so record the lowest weight indicated on the balance. This step can be performed well in advance of all others.
2. Put 1000 mL of tap water in the blender.
3. Tear 4.5 grams of air dry printed copy paper into 2 inch squares and place in the blender.
4. Securely cover the blender and blend for 3 minutes.
5. Transfer the contents to the 2000 mL graduated cylinder. Add 5 mL of the chosen Foaming Agent into the beaker and stir with stirring spoon. Avoid creating foam during stirring.

6. Pour half of the contents into a 1000 mL beaker and label it: FEED sample. Pour the remaining half into another 1000 mL beaker. It is very important to keep the contents well stirred during these transfers; the fibers tend to either settle or rise if not agitated.
7. Stand the unmarked beaker with contents in the plastic tray. **See Figure 1.**
8. Carefully fill the beaker with cold tap water to about 0.5 inch from the top.
9. Stir the contents of the beaker with the large stirring rod or spoon. (The fibers should be evenly distributed in the beaker immediately before the next step.)
10. Connect the air diffuser with the tubing and the air pump and turn on the pump.
11. Place the air diffuser into the bottom of the beaker for 5 minutes. Manually scrape any foam rising above the top lip of the beaker into the plastic tray with your hands or with the stirring rod or spoon.
12. At the end of 5 minutes remove the air diffuser from the blender. The contents remaining inside the beaker represent the accept stream of the process. Label the beaker: ACCEPT sample.
13. The contents of the plastic tray represent the reject stream of the process. Refer to these as: REJECT sample. Add about 100 mL of tap water to the tray and swirl the contents around. Pour the contents into a 1000 mL beaker. Add another 100 mL of water to the tray, swirl and add this to the same beaker. The object of this step is to transfer completely the solids in the tray to the beaker.
14. Filter the FEED, ACCEPT, and REJECT samples onto the pre-weighed filter papers, separately. Before filtering, make sure the samples are well mixed. Try to distribute the solids evenly on the filter paper.
15. Mark off a convenient square area on each of the filter paper samples (same size area for each sample). Use an area that contains approximately 20-50 toner specks in the FEED sample.
16. Count and record the number of visible toner specks in the marked area for each sample.
17. Put the samples in the oven at 105° C and allow to dry for at least 15 minutes.
18. Weigh the samples immediately after taking out of the oven.
19. Determine the weight of each sample by subtracting the dry weight of the filter paper from the dry weight of the filter paper plus solids.

Calculations:

In any contaminant removal process it is important to understand the fiber yield and the contaminant removal efficiency. The following describes how these can be calculated in order to analyze a process. After performing the above-described experiment, perform the following calculations.

There are three ways suggested to calculate the fiber yield.

*Fiber Yield = 100% * ACCEPT Weight / FEED Weight*

*Fiber Yield = 100% * (FEED Weight - REJECT Weight) / FEED Weight*

*Fiber Yield = 100% * ACCEPT Weight/ (ACCEPT Weight +REJECT Weight)*

Each of these weights are of dried solids. Theoretically, without experimental error, they should be equal. This is because the mass balance: "FEED = ACCEPT + REJECT" holds true for all of the following: (1) total material, (2) solids and (3) water. Typically, the first equation is used to calculate yield, especially in a laboratory setting, the other equations can be used as a somewhat independent method, if needed, to verify the results. It should be noted that paper, such as copy paper, is a composite of fibers and inorganic fillers. The fillers, such as clay or calcium carbonate, used to increase the opacity of the paper, can be up to 40% by weight of the paper. Thus, the equations above really measure both fibers and fillers (all suspended solids) in the samples.

A flotation de-inking cleanliness efficiency can be calculated as the following:

Cleanliness Efficiency = 100% (FEED Count – ACCEPT Count)/FEED Count

Cleanliness efficiency is a measure of the percent decrease in contaminant concentration in the ACCEPT sample relative to the FEED sample. The "count" in the equation is typically often expressed as the count of contaminant/unit area. For instance if the dispersed wastepaper fed to a flotation de-inking process has a dirt count of 2000 counts per square meter and the accept sample has a dirt count of 500 counts per square meter, the resulting cleanliness efficiency would be 75%, indicating that the accepts has 75% less dirt concentration than the feed. The cleanliness efficiency is important when evaluating the performance of any contaminant separation process. For example, how might the cleanliness efficiency of a flotation de-inking process change if key operating conditions, such as the time of flotation or amount of foaming agent charged, are changed? In practice, process engineers will evaluate equipment performance based on calculated cleanliness efficiencies and make decisions how to operate the equipment based on the data results.

In order to determine the percentage of the contaminant in the feed stream that is diverted to the REJECT stream a reject efficiency is calculated. The flotation de-inking reject efficiency is defined as the following:

$$Reject\ Efficiency = 100\% \frac{(Mass\ of\ Contaminant\ in\ FEED - Mass\ of\ Contaminant\ in\ ACCEPT)}{Mass\ of\ Contaminant\ in\ FEED}$$

Note that the reject efficiency is not equal to the cleanliness efficiency. The reject efficiency is typically calculated conveniently with the following:

$$Reject\ Efficiency = 100\% \frac{(FEED\ Count * FEED\ WT - ACCEPT\ Count * ACCEPT\ WT)}{FEED\ Count * FEED\ WT}$$

Where WT indicates the dry weight of sample. Note that all of the terms of the above two equations are a concentration multiplied by a weight. If a consistent set of units for concentration and weight are used for all of the terms, these units cancel resulting in a unit of percent. This calculation is simply based on the contaminant mass balance around the process (Contaminant In = Contaminant Out):

$$FEED\ Count * FEED\ WT = ACCEPT\ Count * ACCEPT\ WT + REJECT\ Count * REJECT\ WT$$

The reject efficiency can also be calculated utilizing data on the reject sample as follows:

$$Reject\ Efficiency = 100\% \frac{REJECT\ Count * REJECT\ WT}{FEED\ Count * FEED\ WT}$$

Whether to use the reject or accept characteristics in calculating the reject efficiency is most often based on convenience. It is important to note that both the reject efficiency and the cleanliness efficiency calculations utilize the assumption that the contaminant is evenly distributed in the sample. If the area of sample that is analyzed is not representative of the entire sample, the results will be inaccurate.

Questions

1. Can you think of ways to modify the flotation experiment to increase the removal efficiency of the contaminant? Describe them and test your ideas.
2. Some pulp fiber is scraped away with the foam at the surface of the beaker. How might this be minimized?
3. Very low concentrations of material are sometimes conveniently reported as parts per million (PPM). The PPM of a component is simply the amount of the component divided by the total amount of the sample multiplied by 10^6. It is analogous to using percent to describe a component concentration, in which percent is simply the amount of one component divided by the total amount of the sample multiplied by 10^2. In the paper industry it is common to report the PPM of contaminant in paper on an area basis (rather than mass or volume). It is typically calculated as the fraction of area covered by contaminant divided by the analyzed area times 10^6. Assuming that the toner specks you detected had an average size of 0.01 mm^2 (or use a microscope with a micrometer and find the average size), and using the # specks/area that you recorded, what is the PPM of dirt for your FEED, ACCEPT, and REJECT samples? Often a general quality standard for recycled copy paper is 10 PPM or less. Does the ACCEPT sample meet this criteria?
4. Why would the foaming agent concentration be important? What would be the disadvantage of having too much or too little foam in an automatic continuous system?
5. Can you detect a difference in particle size between the ACCEPT and REJECT samples? If you see a difference, speculate on what might be causing this difference.
6. Do all three methods for calculating the fiber yield agree? Speculate on some of the potential causes for any discrepancy noticed.

Further Activities

1. Investigate the effect of flotation time on the removal efficiency of the contaminant and the fiber yield. Plot the responses (Cleanliness Efficiency and Reject Efficiency) versus time and versus fiber yield and interpret the data.
2. Investigate the removal efficiency of different types of inks or toners using this process using the same type of paper. For instance, print approximately the same image with a ball point pen, a colored

marker, or a pencil. Obtain similar printings from various computer printers (toner based and ink-jet based) and copy machines. Based on the inspection of the inks and toners in the FEED, ACCEPT and REJECT samples, speculate why some contaminants have higher removal efficiency than others. Can you measure the contact angles of water on surfaces made from the toner or inks and use this information to interpret the de-inking results?

3. Investigate the ability of the flotation de-inking process to remove toner from various types of wastepaper. Wastepaper to consider would be copy paper, newspaper, magazines, and printed corrugated containers. For the same conditions, is the fiber yield different for the different types of wastepaper? Speculate why this might be so.

4. Investigate the effect of the disintegration conditions in the household blender on the subsequent contaminant removal efficiency. Develop experiments to determine the affects of disintegrating time, disintegrating speed, and the temperature of the water used in the blender. Investigate the effect of adding the foaming agent prior to disintegrating the sample.

5. Investigate the reproducibility of your dirt count measurements by marking off several separate areas on the FEED, ACCEPT, and REJECT samples and counting the dirt areas in the various areas. The positions of the contaminants on the filter paper should be largely random. Are the differences observed between the FEED, ACCEPT, and REJECT samples significant with respect to the variability of the counting procedure? Why? Referencing an introductory statistic text, can you determine if there is a statistical significance at a 95% confidence level of the dirt counts in the three samples?

6. Can you develop an experiment that determines the foaming ability (volume of foam per unit of air for a given concentration of foaming agent) of different foaming agents? *Samples of industrial foaming agent formulations will be provided by the author on request.* Is the foaming ability of the foaming agents different in water than in a wastepaper slurry? Characterize the foaming ability of several foaming agents and then use the same foaming agents to perform flotation de-inking. Is there a correlation between foaming ability and flotation de-inking efficiency or fiber yield? Hypothesize why there is or is not a correlation. Can you further test your hypothesis? Reference [7] provides more information on foaming agents used in paper recycling and reference [8] provides more general information on surfactants in general.

Instructor Notes: If an oven is not available, air drying the samples over the course of a day or two is reasonable. Note that the moisture content of paper varies with the ambient humidity and this could make samples dried on different days not directly comparable.

CAS Registry Numbers of Chemicals: other than the common dishwashing detergent available at the grocery store, no chemicals are needed.

Safety Warnings:

Care must be taken in operating the blender. Never stick your hand into a blender cup that is installed on the motor. Always blend with the cover on.

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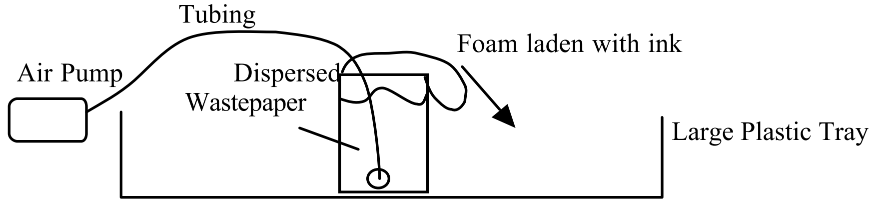

Figure 1. Schematic Drawing of the Laboratory Flotation Experiment.

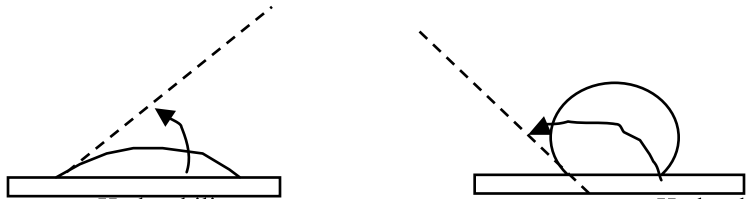

Figure 2. Examples of Water Drops on Hydrophobic and Hydrophilic Surfaces. The contact angle is measured from the surface through the liquid to the tangent of the liquid surface as indicated by the arrows.