Demonstrations and Laboratory Exercises in Aquaculture

II. Activated carbon and ion-exchange in chemical filtration

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This is the second in a series of articles intended for aquaculture educators, or others, that illustrate the principles that impact the field. These can be done as demonstrations or as lab exercises. The authors welcome comments, ideas and submissions from the readers.

Introduction to Filtration

In closed and semi-closed culture systems, water must be treated before it can be recycled into the primary growing tanks and raceways. The nature and degree of treatment is a function of the water quality leaving the growing area, the desired water quality after treatment, and of course the economics of the treatment compared to the benefits. "Treatment" can mean many different things; it may mean aeration, addition of a chemical or drug, degassing, disinfection or filtration.

Filtration can be roughly divided into categories according to what the filter is removing. Some types of filters remove suspended materials, such as leaves and sticks, sediment, pathogens, or the larvae of pests and predators. Other filters remove dissolved materials, which will often not be visible unless they somehow color the water. Filters that remove dissolved materials can themselves be subdivided into either biological filters or chemical filters, according to how they work.

Biological filters are those that use bacteria (usually) to reduce levels of dangerous ammonia; these filters actually remove very little, they primarily convert the ammonia to a less toxic form of inorganic nitrogen, nitrate, by way of a series of oxidation reactions called nitrification. Nitrification filters come in a variety of designs, the best of which maximize the space for the bacteria to grow and keep the bacteria supplied with enough oxygen to do their job. Another type of bacteria-based biological filter reduces the oxidized forms of nitrogen to gas that is nontoxic and can bubble out of the system. These denitrification filters are rather tricky to use and require sophisticated equipment and training. They are, therefore, not very popular in commercial systems. Finally, biological filters can have associated plants or algae that actually do remove (not convert) nutrients from the water, especially inorganic nitrogen.

Chemical filters can also be used to remove dissolved materials (the solutes) from water (the solvent). A foam fractionator is a type of chemical filter that relies on solutes that are only slightly water soluble collecting on the surface of bubbles as they rise through the water. When the bubbles, with their chemical skin, reach the surface, the chemical-rich foam can be skimmed off. Two other types of chemical filters, which are the subject of this article, are activated carbon filters and ion-exchange filters.

Activated Carbon and Ion-Exchange Filters

Activated carbon (or activated charcoal) is a commonly used tool for the removal of organic molecules. The efficiency of the filter depends on a number of factors, especially the solubility of the solute (which itself is related to the length and polarity of the molecules) and the solute's affinity for the activated carbon. The less soluble the molecules are in water, or the greater their affinity for the carbon, the more easily they are removed by the filter. The carbon granules are normally housed in a drum or column. Water passes into the filter housing, through the carbon bed and out the filter exit.

The carbon itself can be produced from a number of substances (wood, nut shells, bone, peat and more). During the manufacturing, there is slow heating of the material in the absence of air to drive out the water and gasses, and to convert the organic forms of carbon to primary carbon. This is followed by the activation step, which can be a heat or chemical treatment that removes the tar and enlarges the tiny pores that are the sites for adsorption of the solutes.

When water enters a filter filled with new carbon, all the carbon's pores are free to remove solutes. At this point, the solutes are largely taken up by the first layer of granules in the filter that the water passes through. But as time goes on, the adsorption sites on those first carbon granules are filled, and the granules deeper in the filter are relied upon to remove the dissolved materials. Eventually, there are not enough adsorption sites in the filter for it to efficiently function, and the carbon must be replaced. (Reactivation of the carbon is possible in theory, but is not practical.) Carbon filters should be placed downstream of biological filters, since free nutrients would stimulate the growth of bacteria on the carbon's surface that in turn would block the pores.

Ion-exchange filters are also used frequently in freshwater aquaculture systems, although unlike activated carbon filters, they are not practical in ion-rich seawater. Recall that, by definition, ions are charged molecules, like Na^+, NH_4^+,

or Mg^{+2} (positively charged cations), or Cl^-, SO_4^{-2} (negatively charged anions). As in the case of the activated carbon filter, this filter material, called the resin, is housed in a vessel that allows water to flow in, pass through the resin bed and flow back out to the primary growing area.

When ion-exchange resins are manufactured, there are particular ions bound to the inert resins. As water with other ions passes through the filter, the ions in the water are captured by the resins, which release the ions that were originally bound to it. For example, calcium (with a charge of +2) can be taken out of the water if it replaces sodium (with a charge of +1) on the resin. It will take two Na^+ ions from the resin to replace one Ca^{+2} ion in the water. There are many different kinds of resins available, depending on the type and charge of the ions that need to be removed. By far the most commonly used exchange resins in aquaculture are the zeolites, a cation exchange material; one of the zeolites, clinoptilolite, can be used to remove NH_4^+ from water.

Ion exchange resins should be used downstream of biological filters since, as discussed above, nutrient rich water would stimulate the growth of bacteria on the resin's surface, blocking ion exchange. They should also be downstream from activated carbon filters and foam fractionation units, since excess nonpolar organic molecules might coat the resin surface, again preventing exchange. However, unlike activated carbon, ion exchange resins can be regenerated so they can be used repeatedly. For example, clinoptilolite can be regenerated with a concentrated NaCl solution, because the Na^+ will replace the NH_4^+ ions.

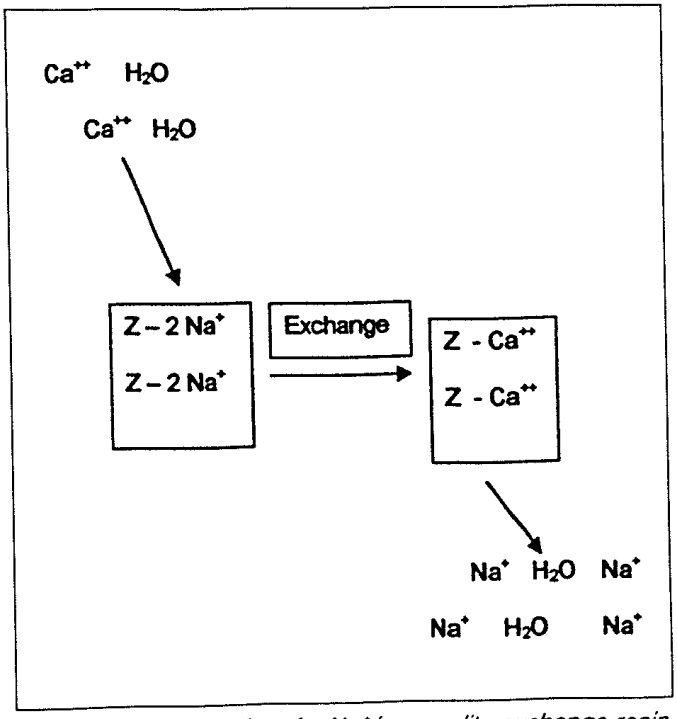


Fig. 1. Exchange of Ca^{++} for Na^+ in a zeolite exchange resin.

Exercise 1 – Adsorption by old activated carbon

This involves the measurement of changes in water color (as a model for organic molecules) as the water passes through an activated carbon filter. The exercise assumes that the students know how to operate a small spectrophotometer. Remind students to use bulbs with the pipettes rather than trying to draw up fluid with mouth suction. The stain in this exercise is one percent acid fuchsin in water. You should wear gloves while making the fuchsin since it can leave red stains on the skin. From this concentrated acid fuchsin you will make a semi-dilute and a dilute solution. Other stains will probably work if this is not available, but you will have to experiment to get the right concentrations.

Weigh out 15 g of granular activated carbon. Be sure that it is washed well with running tap water so that any fine powder is gone. Put the carbon in a 125 ml separatory funnel. Make up a semi-dilute fuchsin stain solution by mixing about 30 ml of tap water with about 50 drops of the concentrated fuchsin stain using a using a disposable Pasteur pipette. Pour this stain into the separatory funnel, which must be closed at the bottom. This should just barely cover the carbon if not, add a bit more semi-dilute stain.


Fig. 2. A small spectrophotometer. Always use the same cuvette, pointed in the same direction, for each measurement, and be sure to wipe the outside of the cuvette before putting it into the spectrophotometer. The spectrophotometer should be "zeroed" with a water blank before each run.

Gently swirl it a few times, and then let it stand for about 30 minutes. (At this point you can begin Exercise 2). After 39 minutes, drain the funnel of the solution, close the funnel again, and add a new solution of the semi-dilute stain (i.e., 50 drops in 30 ml). Let it stand at least another half hour, or when you have finished Exercise 2, whichever takes longer.

Drain the semi-dilute stain solution, and rinse the carbon by pouring tap water through the separatory funnel to remove any remaining stain or carbon powder. Now, using this old activated carbon, repeat the procedures with the dilute stain outlined in Exercise 2, recording the data in Table 1 and on Figure 4.

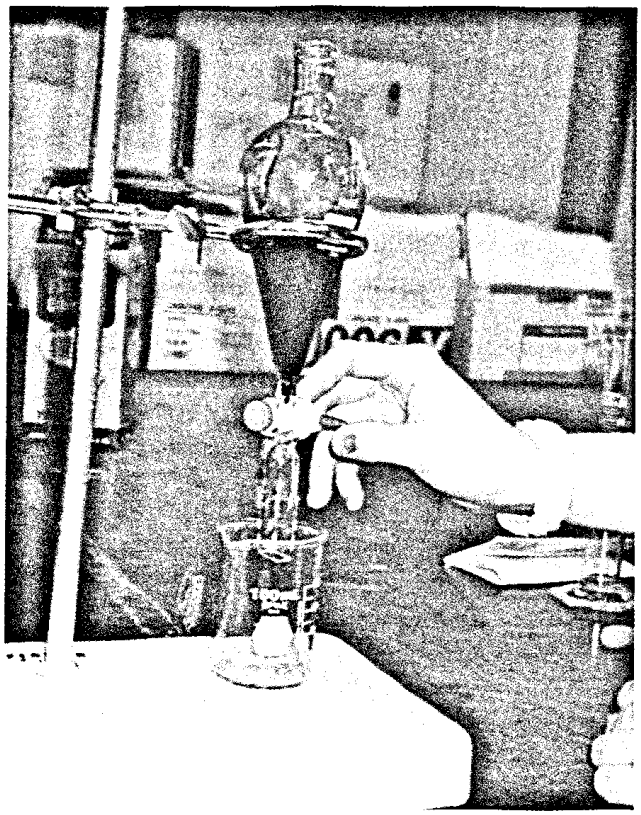
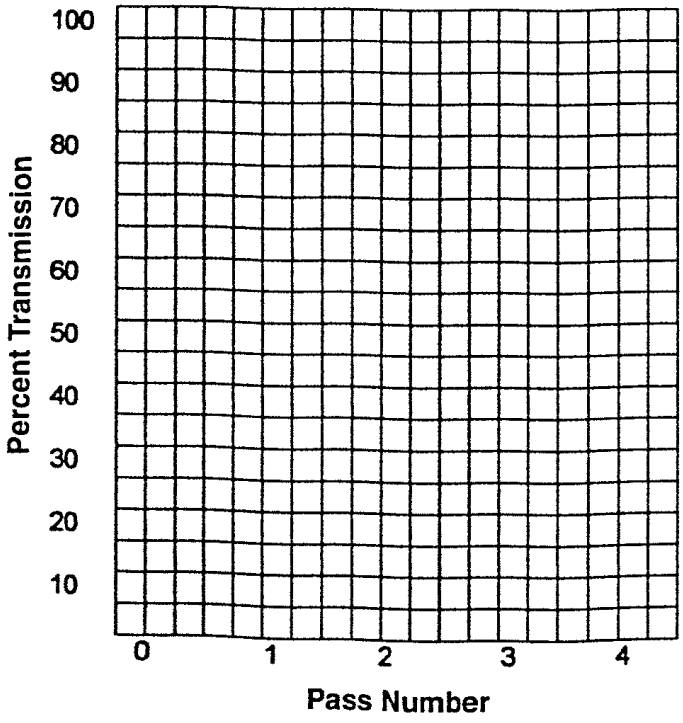


Fig. 3. A separatory funnel with activated carbon.

Table 1.

	Percent trasmission Exercise 1 "old carbon"	Percent transmission Exercise 2 "new carbon"
Fresh stain solution		
Stain solution after one pass through the carbon		
Stain solution after two passes through the carbon		
Stain solution after four passes through the carbon		

Figure 4.



Exercise 2 – Adsorption by "New" Activated Carbon

As in Exercise 1, weigh out 15 g of granular activated carbon, wash it with running tap water so that any fine powder is gone, and put the carbon in a 125 ml separatory funnel. Do not bathe the carbon in a semi-dilute stain solution as you did in Exercise 1.

Make up a dilute stain solution by adding about 10 drops of the fuchsin stain to about 40 ml of tap water. Using a spectrophotometer, measure the percent transmission of the stain solution at a wavelength of 540 nm, and record your results in Table 1. Then pour the solution through the carbon while the funnel is closed. Open the bottom of the funnel slowly so that the outflow is about 2 to 4 drops per second, and collect the outflow in a small beaker. Measure the percent transmission of this fluid and record the value, then add the same diluted stain that has already passed through the filter once into the filter again. Repeat this procedure three more times, each time recording the percent transmission. When the values are all collected, graph the data on Figure 4.

Student Question : Compare the results of Exercises 1 and 2. Discuss this comparison.

Answer: In Exercise 1, using the old carbon, the adsorption sites had mostly been filled by the concentrated stain before the dilute stain solution was used. Therefore, there was less change in the percent transmission of the dilute stain solution after each pass than in exercise 2. Carbon like this is of little value in an aquaculture system and must be changed before it reaches this state.

Student Question: Based on the data collected in Exercise 2, calculate the four ratios below. If there are differences in the ratios, explain what you think is happening.

- [percent transmission of fresh stain solution] ÷ [percent transmission after the first pass] =
- [percent transmission after the first pass] ÷ [percent transmission after the second pass] =
- [percent transmission after the second pass] ÷ [percent transmission after the third pass] =
- [percent transmission after the third pass] ÷ [percent transmission after the fourth pass]=

Answer: The first ratio should be the smallest. Before the stain is poured through the filter for the first time, the number of available solute molecules is greatest (giving the lowest percent transmission), and the number of free adsorption sites on the carbon is greatest. As the number of sites on the carbon decreases, and the number of solute molecules decreases, the differences between passes must decrease.

Exercise 3 – Removal of Ammonia by Zeolite

Students will need test kits for measuring ammonia; several inexpensive and easy to use kits are available from commercial sources. Make up a working stock of ammonia by dissolving about 38.2 mg of NH_4Cl in a liter of water (about 10 mg N per liter).

Put 5 g of zeolite into a 125 ml separatory funnel. Add 20 ml of distilled water to the closed zeolite column; open the column slowly, until the flow is one drop per second or less and collect the water at the bottom in a small beaker. Use your test kit to measure the amount of ammonia, if any, that is present. Record the results on Table 2.

Measure the amount of ammonia in the stock solution. Record the results on Table 2. Now pass 20 ml of the ammonia stock solution through the zeolite resin, again letting it flow out at about one drop per second, and collecting it at the bottom; measure the amount of ammonia present in the solution and record the results.

Table 2

	Ammonia present
Distilled water	
Ammonia stock solution	
Ammonia stock solution after one pass through the zeolite	
Ammonia stock solution after two passes through the zeolite	
Ammonia stock solution after three passes through the zeolite	

Pass 20 ml of fresh ammonia stock solution through the resin, again letting it flow at about one drop per second, and collecting it at the bottom. Take the collected fluid and pass it through the resin a second time, then measure the amount of ammonia present in the solution and record the results on Table 2. Repeat this with another 20 ml of fresh ammonia stock, but this time let it pass through the column three times before the ammonia is measured and recorded.

Student Question : Draw a picture of what is happening at the chemical level when the ammonia solution is passed through the zeolite resin bed.

Answer: The drawing should be similar to Figure 1, but in place of Ca^{++} and Na^{+} at a 1:2 ratio, the student should draw NH_4^+ and Na^{+} at a 1:1 ratio. Students should also understand that it's the ion NH_4^+, not NH_3 that is exchanged. However, this will mean that NH_3 is also reduced because the NH_3 - NH_4^+ equilibrium is maintained.

Student Question: What happens as you increase the number of times that water with ammonia is cycled through the filter?

Answer: The more passes through the zeolite, the more ammonia is eventually removed.

Exercise 4 – Removal of Ammonia by Zeolite in the Presence of Salt

Make up a 20 percent NaCl solution by completely dissolving 20 gm of NaCl in 100 ml of distilled water.

Take 20 ml of the standard ammonia solution and dilute it with 20 ml of distilled water. Mix the 40 ml of diluted standard and measure the amount of ammonia present. Take 20 ml of the dilute solution, pass it through the zeolite resin bed slowly as before, and measure the ammonia present. Record the results in Table 3.

Now take 20 ml of the standard ammonia solution and dilute it with 20 ml of 20 percent NaCl. Measure the amount of ammonia present. Take 20 ml of this solution, and pass it through the zeolite resin bed as before. Measure the ammonia present, and again record the results.

Table 3

	Before column	After column
Ammonia stock solution and distilled water (1:1)		
Ammonia stock solution and 20 percent NaCl (1:1)		

Student Question: Why did you get the results you did in exercise #4, and what are the implications for aquaculture?

Answer: When ammonia was passed through the column in the presence of salt, the zeolite is much less efficient at removing the ammonia because there was competition between the two monovalent cations, Na^{+} and NH^{+} for the sites on the resin. This suggests that this type of ion exchange material cannot be used effectively in saltwater aquaculture systems.

End Note

These exercises may be copied for use in classrooms or other educational environments (copyright law still applies) without prior permission from the authors. We would appreciate receiving comments about these exercises. We thank B.J. Landau for her comments on this manuscript.

Auhor Notes

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