

Granular Activated Carbon

IF AT FIRST YOU DON'T SUCCEED

... TRY, TRY AGAIN

By Charles "Chubb" Michaud

This is Part II of a three-part series on Granular Activated Carbon.

In the sense that the term "water" cannot be used to describe a single starting point composition, neither can the term "granular activated carbon" be used to define a single chemical entity. It is, rather, a generic name for a class of chemical adsorbents. If one type of GAC is tried for a particular application and comes up short, it would be reasonable follow-up to try another type of GAC with differing properties.

In Part I of this series, we described the GAC manufacturing process and gave ranges of GAC properties used for water, vapor phase and waste applications. Part II will delve more deeply into the mechanisms by which GAC works and look at the effect of variables such as contaminant type and concentration, temperature, pH and flow rate, as well as some of the variables presented by GAC itself.

A Matter of Time

Earlier we looked at a simple graphic relationship between GAC and contaminant concentration vs retention time to describe a concept we called "half length".

From this simple relationship we can draw several parallel conclusions:

1. The completeness of the GAC reaction mechanism is a function of time.

2. The kinetics of the GAC reaction mechanism are driven by contaminant concentration.

3. The "leakage" of the GAC

reaction is a function of both time and concentration.

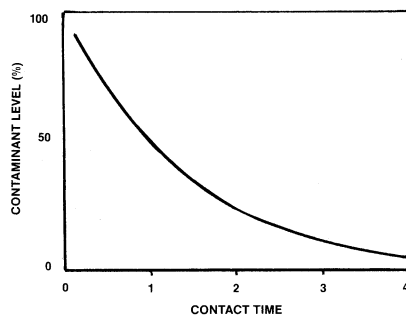


Figure 1.
Removal vs Contact Time

MECHANISMS OF GAC FUNCTION

1. Adsorption

All molecules exhibit attractive forces for one another. A clean carbon (non-polar) surface such as that of GAC has a particularly strong attractive force for other non-polar materials. If those attractive forces are greater than the forces that keep those materials dissolved in solution, then those materials will adhere (adsorb) onto the GAC surface. Remember that water consists of a hydrogen (H⁺) and a hydroxyl (OH⁻) ion and is therefore very polar. It is this difference (in this case, opposites do not attract) between polar and non-polar that forces select contaminants to preferentially adhere to the GAC. Adsorption, although not unique to GAC, remains the primary mechanism with which we are

concerned.

Non-polar materials are those that are either non-ionized or very weakly ionized in aqueous solution. Examples are organics such as solvents, pesticides, tannins, greases and oils. Tannins, which are organic acids, have slight ionization and are highly soluble in water (compared to benzene or gasoline).

In general, the less soluble an organic in water, the more readily it will be adsorbed by GAC. Conversely, the more soluble it is, the more difficult it will be to adsorb because high solubility means that there are very strong forces keeping that particular substance in aqueous solution.

Let us take a look at common alcohols, their solubility and relative adsorbability onto GAC. Table I gives the values:

Note that as molecular weight increases, solubility decreases and equilibrium adsorption increases. The same is basically true for aldehydes, amines, aromatics, esters, ethers, glycols, ketones, organic acids and organic oxides.

It would appear that the predictability of adsorption would be quite simple. All one has to do is run an adsorption equilibrium curve for every conceivable contaminant, at four or five contamination levels, to various end points, at differing temperatures and pH's and in all combinations in waters of varying ionic strength!! And we haven't even considered different mesh sizes of GAC. Obviously, not so simple, especially when you consider the dozens of different GAC products—each of

<u>Alcohol</u>	<u>Molecular Weight</u>	<u>Aqueous Solubility (%)</u>	<u>Adsorbability gms/gm GAC</u>
Methanol	32.0	infinite	0.007
Ethanol	46.1	infinite	0.020
Propanol	60.1	infinite	0.038
t-Butanol	74.1	infinite	0.059
Isobutanol	74.1	8.5	0.084
n-Butanol	74.1	7.7	0.107
n-Amyl	88.2	1.7	0.155
n-Hexanol	102.2	0.58	0.191

Table 1—Adsorbability of Alcohols

which will give different results.

How then does one arrive at the “proper” design for a GAC system? Unfortunately, that would be impossible to describe in this text—even if we occupied space in the next 500 issues. However, if we apply good logic and conservative practices to what is already known and what we believe to be, along with the effects of variables and the risk assessment of “what happens if we’re wrong?!!”, we can usually arrive at a workable design. Let’s examine some of these variables.

First off, adsorption is a multi-step process. Contaminants must first move through the bulk solution to the surface of the GAC. This is best accomplished in a column or “bed” in which the solution passes through a packed layer of GAC. Although similar effects can be obtained by “batch” processing (mixing a quantity of GAC with solution, then filtering), column applications lend themselves more readily to continuous processes and higher GAC utility. We shall therefore limit our systems only to column applications.

We have provided the mechanism (flow) to bring the contaminant into contact with the GAC. What happens next? Now, the contaminant must diffuse into the GAC pore structure. The larger the molecule, the slower the diffusion. The faster the flow rate, the more apt the particle is to be swept away. The smaller the GAC pore structure, the more difficult it is for the compound to diffuse into that pore. The more contaminant present, the higher the probability of it entering the pore.

Since the majority of the surface area suitable for adsorption is within the pore structure, allowing sufficient time for diffusion cannot be over emphasized. Once inside the pores, the contaminant diffuses toward the more highly attractive micropores until finally, the attractive forces overcome the forces holding the compound in solution and we have

adsorptive attachment. Depending upon equilibrium, the adsorbate may be one or several molecules deep.

Once adsorbed, these compounds cannot be desorbed by mechanical means such as backwashing. However, if a force stronger than the adsorptive force comes along, the sorbate can be displaced. Examples of such forces could be an improved solubility due to pH shift, increased volatility due to increased temperature, competition for adsorptive surface by a compound of higher attractive driving forces, or destruction of a compound by bacterial action, producing byproducts of lower attraction.

Adsorption vs pH

Most organics are more soluble on the alkaline side than on the acid side. This means that they are more readily adsorbed at lower pH's than high pH's. If we increase the size of the GAC bed by 20% for every pH point above 7.0, we'll be going in the right direction.

Adsorption vs Temperature

In general, lower temperatures favor adsorption while higher temperatures favor desorption. In aqueous applications the temperature effect is offset by the increased diffusion rate due to a decrease in solution viscosity with increasing temperature. However, watch out for low boilers which may come unglued much beyond 100°F. In general, if the compound has a boiling point below 150°F, increase the size of the bed by 20% for every 10°F above 100°F. If the boiling point is greater than 150°F, increase the size of the bed by 20% for every 10°F below 70°F.

Adsorption vs Contaminant Type and Concentration

Higher molecular weight, larger molecules of marginal water solubility are more readily adsorbed than smaller,

more highly volatile, water soluble ones. Where a mixture exists, we must design for the more difficult to remove portion. The presence of a few ppm of high molecular weight natural organics such as fulvic acid, can reduce GAC capacity for the more volatile organics by 50% or more. Use caution and get a good analysis.

Higher concentrations provide higher diffusion driving forces and produce higher capacities, but also require longer retention times and give higher leakages. GAC considerations should be limited to a few hundred parts per million or less unless provisions are made to “regenerate” in place. Even then, a practical upper limit would be 1000 ppm.

Adsorption vs GAC Particle Size

Smaller GAC particles allow more effective contact. Therefore, higher flow rates may be utilized (or smaller beds). However, pressure drop increases. A 20 x 50 mesh GAC may exhibit two to three times the kinetic removal of a 12 x 40 mesh GAC and 10 to 20 times that of an 8 x 30 mesh GAC. Reserve the use of finer mesh (20 x 50) GAC for critical applications such as removal of toxic substances from drinking water or very small systems such as cartridge filters.

Adsorption vs GAC Type

Organics generally do not care what the lineage of a GAC particle is. However, they do care about the general pore size, shape and distribution; and the original raw material does play a role here.

It is a common misconception to judge a GAC's expected performance on Surface Area alone or an Iodine Number alone. In one application GAC “A” may outperform GAC “B”, and in another they may reverse.

It is not surprising to find that reactivated GAC's may sometimes

perform better than virgin products because of a change in the pore size distribution with reactivating. On the other hand, reactivation may all but completely destroy certain performance characteristics if these characteristics come from the micropore of the GAC.

All GAC's contain some pores in all size ranges. Therefore, all GAC's can do all jobs. However, matching the pore size and distribution of the GAC to the intended use will result in a higher utilization of money and equipment. Again, it is very important to know what contaminants are present and try to match their chemistry to the "proper" GAC.

Adsorption vs Retention Time

As always, the higher the retention time, the more complete the adsorption for any given set of circumstances. The nature of the impurity, the influent concentration and the intended use of the effluent will dictate the total percent removal of that impurity that is required. For any given GAC, adsorption can be improved with longer contact time.

Summary

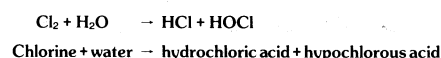
We have devoted a considerable amount of time and space to discussion of adsorption. The adsorption properties of GAC at a reasonable cost is what gives GAC its broad utility in water treatment. Later, we will look at typical design parameters for adsorption applications and provide tables of relative adsorbability of hundreds of compounds.

Adsorption with GAC is affected by time, temperature, pH, particle size, type and concentration of contaminant and the GAC itself.

The second most important application for GAC involves Catalytic Reduction. This is the mechanism by which free chlorine, hydrogen peroxide and ozone are "removed".

2. Catalytic Reduction

Chlorine has long been used as a disinfectant for public water supplies. Chlorine may be added as Cl₂ gas or as sodium or calcium hypochlorite at levels of 0.5 to 5 ppm with the intent of having residual of approximately 0.1 ppm reaching the home or plant site. The reaction of Cl in water is:



It is the presence of the disassociated HOCl that gives us the active free chlorine as hypochlorite ion (OCl⁻).

GAC has long been used for the removal of free chlorine. Dechlorination is not the adsorption phenomena which occurs with organic compounds. Dechlorination is actually a chemical reaction whereby HOCl reacts with the GAC surface and the carbon is oxidized:



Where CO* represents an oxide of carbon. The chlorine becomes a non-oxidative chloride ion.

GAC reacts readily with free chlorine and has a usable capacity of 2—3 lbs. of chlorine per lb. of GAC. Half length for a typical dechlorination reaction is a few seconds with 99% completion in less than 60 seconds. For this reason, if a GAC has been designed for organic removal (requiring several minutes retention time) it generally has been oversized for dechlorination.

The most important design consideration for dechlorination is pH. Below a pH of 7, free chlorine exists primarily as hypochlorous acid. GAC is very effective here. Above a pH of 8.5, chlorine exists primarily as the hypochlorite ion. The removal rate is much slower and it may require three minutes or more to achieve a 99% reduction. If you install GAC for dechlorination on a water supply with a seasonally fluctuating pH, don't be surprised to get "premature" break-through when the pH rises.

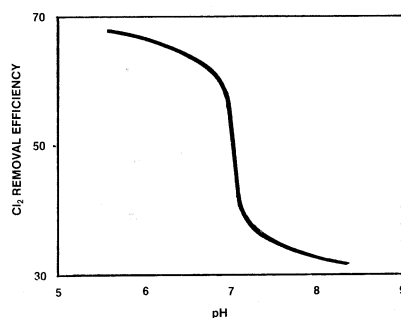


Figure 2.
Chlorine removal vs pH

The second most important design consideration for dechlorination is temperature. For every 20°F rise, the reaction rate doubles. Allow the winter-time temperature drops by designing for the coldest operating conditions.

A third design consideration for dechlorination is particle size of the GAC. The smaller, the better. However,

since flow rates with GAC for dechlorination tend to run quite high, pressure drop may again be the limiting factor.

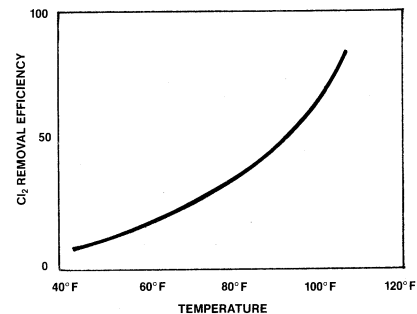


Figure 3.
Chlorine Removal vs Temperature

A 12 x 40 mesh GAC can be run at twice the flow rate of an 8 x 30 mesh GAC and produce a similar break-through capacity curve. A 20 x 50 mesh GAC can be run at more than twice that of a 12 x 40.

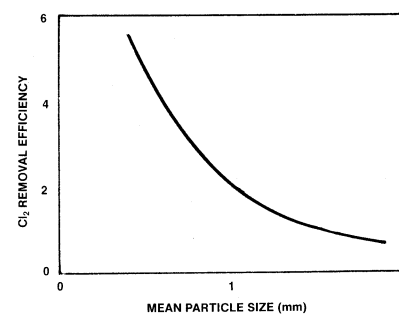


Figure 4.
Chlorine Removal vs. GAC Particle Size

Total capacity for dechlorination is a function of flow rate. This would be our fourth consideration. For a 12 x 40 mesh GAC, we can handle five times the influent concentration by cutting the flow rate in half. Also, we can handle nearly 10 times the total throughput (gallons) at a constant Cl₂ concentration with a 50% reduction in flow rate.

The removal of hydrogen peroxide and ozone with GAC is similar to that of free chlorine. Again, GAC reacts with the free oxygen. In fact, GAC will remove dissolved O₂ from water and is being used commercially for industrial deoxygenation of boiler feed water.

A word of caution when working inside a GAC tank. GAC also depletes O₂ from the air. It is necessary to provide good ventilation or supplemental breathing apparatus.

Although GAC would be an excellent method of removing free fluorine from

water, it should be pointed out that fluorine usually does not exist as "free" F_2 but rather as the fluoride ion. GAC is ineffective in removing most water soluble salts.

Chloramine Removal

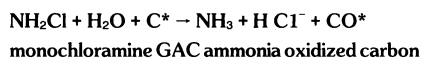
Hypochlorous acid, HOCl, is a very strong oxidant. As such, it can readily react with various organics in water to form trihalomethanes (THM's). THM's have been shown to be carcinogenic in animals and are suspected to be at least mutagenic in humans. The EPA has placed upper limits on THM concentrations in drinking water. High doses of free chlorine for disinfection tend to produce unacceptable levels of THM's.

The addition of ammonia to chlorinated water forms a more stable, somewhat less reactive antibacterial oxidant called chloramine. While chloramines are less prone to forming THM's, they have a drawback that requires their complete removal. Chloramine can transfer its positive chlorine to other amines such as protein, which can cause hemolysis in dialysis patients. Chloramines are also particularly harmful to fish. For safety, chloramine must be reduced to concentrations of less than 0.1 ppm. It should be pointed out that the more stable chloramines are less efficient disinfectants than chlorine and do require higher concentrations to be effective. Concentrations as high as 3 ppm have been reported and the minimum found to produce clinical symptoms is only 0.25 ppm.

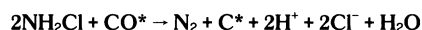
Chloramines pass through reverse osmosis membranes but GAC has proven very effective for removal.

Chloramines pass through reverse osmosis membranes but GAC has proven very effective for removal.

Chloramines can be either monochloramines (NH_2Cl) or dichloramines ($NHCl_2$). The "di" reacts very rapidly with GAC. However, the "mono" is very slow:



Once the surface oxides have built up on the carbon, the ammonia by-product converts to nitrogen in subsequent reactions:



At equilibrium, retention times of nearly 30 minutes are required to reduce NH_2Cl from 2.8 ppm to 0.1 ppm. However, early in the life of the

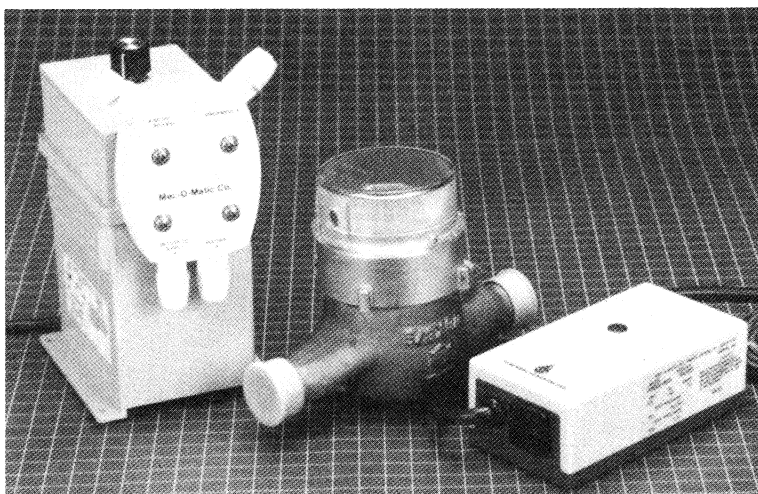
GAC bed, much better kinetics are enjoyed. Retention times of two to three minutes will reduce NH_2Cl levels from 2.8 to 0.1 ppm for approximately 20,000 BV (bed volumes) or about 150,000 gal/ft. (12 x 40 mesh coal based GAC.)

Summary

The "half length" concept dictates that a certain percentage of chlorine will be removed in a certain length of time, corrected, of course, for temperature, pH and GAC particle size. To design a bed to that exact size would

work well — for a week or so. Reserve capacity must then be built in so that there is adequate additional bed to replenish the GAC that is "used up" or backwashed out. Depending upon the safety factor one needs for "risk" insurance, the additional bed volume may be as little as 50% (for general purpose drinking and bathing) to 500% (for dechlorination of aquarium feed waters for very rare and expensive tropical fish). The extra volume is usually designed into the "depth" of the bed rather than the diameter. The extra straight wall for a GAC tank is

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relatively inexpensive. As we pointed out earlier, doubling the bed volume for a given flow rate may increase the life of the system by 1000%.

3. Particulate Filtration

A packed GAC bed, because of the irregularity of the granules and high pore volume, is an excellent filter for suspended particles, debris, silt, colloids and even bacteria. Regular and rigorous backwashing will remove much (but not all) of this trapped material. GAC would be expected to be more efficient than a sand filter or a depth filter for fineness of particles removed. However, this aspect of GAC performance should be considered only as a fringe benefit above and beyond its use for adsorption or reduction. We do not recommend using GAC as a particulate filter where heavy loading is anticipated and the maintenance of high adsorptivity or dechlorination is required.

The pores of GAC can be easily plugged or blinded by heavy particulate loadings. This would seriously affect the GAC's capacity and kinetics and may lead to channeling and the need for frequent backwashing. Backwashing can lead to a dirt build-up on the wrong end of the filter unless dual beds are used.

It is ok to use GAC in water of high turbidity. However, you should monitor the pressure drop and removal performance closely to be assured that the GAC is still working. Consider a prefilter ahead of the GAC and use the GAC's filtration characteristics only for polishing.

4. Ionic Paring (Plating)

While, as a general rule, GAC is not effective for the removal of soluble salts, there are exceptions. Molybdates, gold chloride, silver salts, chromium and various cyanide complexes adsorb very well. In fact, GAC is one of the primary adsorbants for the recovery of gold and other precious metals from leach solutions.

The mechanism employed here is similar to cathodic plating. Heavy metals in solution actually plate out on the surface of the GAC. Removal or stripping is done by chemical means with the metals recovered as a concentrate.

While most of the GAC's used here are vapor phase, that is, very high activity products with a large number of small pores, water carbons work well also.

High Sorption Potential	Antimony Arsenic Bismuth Chromium Gold Tin Silver
Moderate Sorption Potential	Mercury Cobalt Zirconium
Fair Sorption Potential	Lead Nickel Titanium Vanadium
Low Sorption Potential	Iron (as Fe+3) Iron (as Fe+3) Zinc Cadmium Beryllium Copper Barium Selenium Molybdenum Manganese Tungsten

Table 2—Metal Sorbability by GAC

Complexed metals generally adsorb better than the straight ionic species. Organic complexes are even better. Table 2 lists several metals as examples and rates their relative adsorbability.

The real plus on this aspect of GAC performance is that in waters that contain traces of mixed industrial waste or mine drainage contamination, GAC is the only product needed to reduce heavy metals and organic. GAC, for instance, would be a good choice to investigate for lead removal.

Design parameters for metal removal are generally generous (1—1.5 gpm/ft³). Don't try to treat a whole house with a 10 inch cartridge.

5. Molecular Filtration

The relative adsorbability of one substance over another makes it possible to actually separate mixtures of organics by passing them through a bed of GAC. This is of little importance to water treatment where the intent is really the complete removal of all contaminants as a group.

Applications For GAC

We have looked at GAC history and production in Part I and have covered mechanisms and variables in Part II. In part III, we will look at the design considerations for:

- A. Dechlorination
- B. Chloramine removal
- C. Taste and Odor reduction
- D. General Organic removal
- E. Toxic Organic removal
- F. Radon Gas

In addition, a table listing many of the common contaminants found in water supplies will be prepared giving the relative ease or difficulty of removal.

Additional Glossary Terms

Block Carbon—Powdered carbon that has been pressed into a solid block, usually with the aid of a binder or "glue". The purpose is to provide a very highly available carbon surface (high kinetics) with excellent micron or sub-micron filtering capabilities. Reportedly will filter out bacteria and even some viruses.

Column—Also known as a "bed" of GAC or a "contactor." A tank, usually vertical, with an inlet at one end and outlet at the other with some means of holding layers of media in place so water can be "filtered" through it.

Desorption—The opposite of adsorption. This is something we try to avoid when employing GAC for organic removal.

Continued on page 50

GAC:

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Diffusion—Migration of a molecule or particle from an area of higher concentration (water phase) to an area of lower concentration (pores of GAC).

Efficiency—Often linked with capacity. Used to define the completeness of adsorption removal.

Kinetics—Refers to the rate at which a reaction proceeds. The rate of reaction is tied more closely to the efficiency of GAC performance rather than its capacity.

PAC—Powdered activated carbon.

Reactivate—In the case of GAC, to “reburn” spent GAC to remove organics and restore adsorptive capacity. Partial reactivations may be accomplished with steaming, hot water, acid or caustic treatments to cause adsorbed or trapped contaminants to desorb. Expect 10–20% loss of capacity on reactivation due to attrition losses. Actual capacity per cubic foot of

recovered GAC may not change drastically.

Silver Impregnated Carbon—GAC that has had oligodynamic silver plated onto its surface to serve as a bacteriostat to prevent bacterial growth in filters.

Charles “Chubb” Michaud is president and founder of Systematic Co. and its parent, Coast Filter Media Supply Co., Inc. with offices located at 1219 W. Imperial Hwy., Brea, CA 92621. (714) 680-8321.

PERSONNEL:

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make the evaluation a constructive process.

Try to persuade him to talk. Ask questions about recent events that he can talk about easily. A recent, successful sales call often represents a good topic that can encourage the sales person to

relax.

Then, start your evaluation by emphasizing the positive aspects of his performance. That will help dispel the presumed threat in the evaluation process. Then, as the sales person relaxes, you can go on to the constructive part of the review.

The final stage in the evaluation involves another look at the job description that includes each sales person’s objectives. Mutually discuss the positive and negative aspects of your evaluation. Develop some mutual agreement about any changes in the objectives set forth in the sales person’s job description. His participation in the process increases the sales person’s commitment to achieving the objectives selected.

After using an effective evaluation system in your water treatment business for six to twelve months, you should start seeing the benefits on your firm’s bottom line. Moreover, you will find better morale among your sales people. They will become more motivated to continuing building on their success in sales.

At the same time, implementing an effective evaluation program will make you feel better about your role as the firm’s sales manager. Helping sales increase and people grow makes a sales manager a success.

Bill Stiles is a National Selling Champion. He has been sales manager and marketing vice president of a multi-million dollar marketing firm. He lectures frequently on sales management, self-improvement, and the principles of selling and has authored many articles and books on selling.

NEGOTIATING:

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Don’t be afraid to be aggressive when you’re negotiating, but always have your plans well-prepared,” concluded Dr. Mendonsa. “And most of all, remember that emotional reactions are the enemy of a good negotiator. Keep your emotions under control and you’ll get a better deal.

For more information on business negotiation, IDNI offers a free information package. Contact: Ms Cynthia Williams, Dept. 5037, IDNI, P.O. Box 882, Red Bluff, CA 96080 (916) 529-0276., ext. 5037.

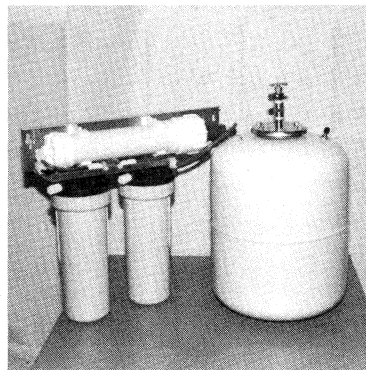
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