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THE USE OF POWDERED ACTIVATED CARBON ADSORPTION FOR COLOR REMOVAL

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Abstract

In this investigation, two separate carbons are evaluated to determine whether they are capable of removing color from paper mill effluent, named Mill A. The two carbons are from Westvaco and from the Kalamazoo Water Reclamation Plant.

The experiment consisted of adding 250 mg carbon of 250 ml of effluent and determining whether, after vacuum filtration, the color was removed using a spectrophotometer. The results proved positive and color was removed in all samples, and with both carbons.

After the initial experimental procedure one of the carbons were chosen, Westvaco, and percentages of the 250 mg of carbon were taken. The carbon was added to the 250 ml of effluent and the experiment was run as usual. This data was essential for an isotherm study.

After plotting the isotherm graph it was evident that at 100 mg carbon per 250 ml of effluent the carbon was able to remove the color. The 100 mg was used in the determination of the amount of carbon needed for two carbon systems based on a 2 million gallon per day effluent stream.

The two types of carbon systems considered are a primary clarifier addition system and a carbon bed system. After analysis of the costs of equipment and carbon costs it became evident that the carbon bed system is the more economical system.

INTRODUCTION

Most paper manufactures are located on major waterways where they have access to large, uninterrupted volumes of water that are used for paper production and then typically discharged back into the waterway as waste.

During the last two decades, as a result of increasing concerns for the environmental impact of industrial effluent discharges and the increasing cost of effluent treatment, there has been increasing emphasis on water conservation and reuse in the pulp and paper industry.

Problems arise when trying to determine an efficient, cost effective means of cleaning the water that is being reused over and over again. There are several different types of advanced waste water treatment methods such as chemical clarification, recarbonation, filtration, disinfection, and demineralization, etc. However, the one that is of interest here is activated carbon adsorption.

Activated carbon is the greatest developed and one of the most efficient processes available for the removal of most organic and some inorganic materials from wastewter. Activated carbon is also capable of removing color from water.

A papermill named produces colored paper and therefore produces colored effluent. The papermill is considering closing their water loop in order to lower water usage costs. In closing their water loop it will be necessary to remove as much of the remaining color as possible. Color water is necessary in order to eliminate any interference with colors, organics, and inorganics.

Activated carbon is capable of removing both organics and inorganics, however, color removal by way of activated carbon adsorption is yet to be established.

Two different carbon samples were obtained (one used for color removal and the other primarily used in waste water treatment facilities to remove organics and inorganics) to determine whether color can be removed from the effluent samples as well as a determination of which carbon is more desirable. From the results of the experiments two carbon systems will be considered and evaluated for cost effectiveness. The first carbon system will consist of carbon addition into the primary treatment area and the second system will consist of a separate carbon system using columns.

BACKGROUND

The paper machine is the largest user of water at a pulp and paper manufacturing facility. Consequently, over the years numerous programs aimed at closing machine water systems by reducing fresh water input into paper machines have been proposed and implemented.

Treatment of machine white water by removing fibers and suspended solids and reusing the treated water at a location where the quality needs are consistent with the quality of the supplied water have been used widely for substituting fresh water with recycled white water from paper machines.

Major examples of water reuse in the paper mill include: recycle of white water as the main source of dilution water use outside of the headbox loop, use of filtered white water in most showers, use of temperature controlled filtered white water as a vacuum pump seal water, and return of contaminated white water streams to process uses nearer their origin.

In Little Falls, Minnesota Hennepin Paper Company initiated a Zero Discharge Program in 1990 to eliminate wastewater discharge to the Mississippi River by installing a closed-loop wastewater recycling system and a carbon filter for the advanced water treatment operation.

The Zero Discharge Program's closed-loop recycling system eliminated the annual discharge of about 562 million gallons of wastewater; 149,000 pounds of total suspended solids; and 57,000 pounds of biochemical oxygen demand.(Case Study)

Some of the reasons paper mills consider closing their white water loop is to reduce the amount of fresh water use in the mills processes, to reduce the amount of total suspended solids which are disposed of, to conserve water and reduce the dependency on river water, to prevent environmental regulatory problems, and finally to improve their public image.

There are also problems encountered in recycling or reusing white water. Among the problems that have been identified are: (1) increase in white water solids, (2) increase in corrosion, (3) nozzle plugging, (4) increase deposits formation, (5) biological growth, (6) elevated white water temperature, and (7) product quality impacts.

One such means of decreasing all of the negative impacts listed above along with the removal of color from white water is the use of activated carbon adsorption.

Activated carbon had been introduced into the paper industry in the early 1980's. Experiments which involved the use of activated carbon adsorption include such experiments as; the use of carbon in color removal (however, that experiment also consisted of a microlime treatment in conjunction with carbon), the use of activated carbon in treating E stage filtrate from a bleached kraft mill, the addition of activated carbon to an activated sludge treatment system of pulp mill effluents, and most recently the effectiveness of two commercially available powdered activated carbons were examined in removing total organic carbon, total organic chlorides, and organic chlorides with molecular weight less than one thousand.

Activated carbon has not been looked at seriously, in an actual mill environment since the early 1980's which is why the topic needed to be evaluated once again.

In understanding adsorption by activated carbon it is essential to know that activated carbon removes some organic and inorganic material from water by the process of adsorption or, the attraction and accumulation of one substance on the surface of another. In general, pore structure and high surface area are the most important characteristics of activated carbon in adsorption of material from water and the chemical nature of the chemical nature of the carbon surface is less important.

There are several factors which affect adsorption by activated carbon, including (1) characteristics of the activated carbon; (2) characteristics and concentration of the material to be adsorbed; (3) characteristics of the wastewater, such as pH and suspended solids content; and (4) the contacting system and its operation.

Most of the surface area available for adsorption by carbon is located in the pores within the carbon particles created during the activation process.

Activated carbon can be made from a variety of carbonaceous materials including wood, coal, peat, lignin, nutshells, bagasse (sugar can pulp), sawdust, lignite, bone, and petroleum residues. In the past, carbons used in industrial application have been produced most frequently from wood, peat, and wastes of vegetable origin. The present tendency in the manufacture of granule carbon for wastewater treatment purposes is toward use of various kinds of natural coal and coke, which are relatively inexpensive.

Among the major U.S. producers are:

Calgon - "Filtrasorb" granular carbons
Westvaco - "Nuchar" granular carbons;
            "Aqua Nuchar" powdered carbons
Husky Industries - "Husky" powdered carbons
ICI United States - "Hydrodarco" powdered and granular
Barneby Cheney - granular and powdered carbons
Union Carbide - "Columbia" granular carbons
Witco Chemical - "Whitco" granular carbons

Activated carbon can be classed in two groups: powdered and granular. In wastewater applications, powdered carbons are predominantly (60-75 percent) smaller than 325 mesh, while granular carbons are typically larger than 40 mesh. Powdered activated carbon is usually produced by activating lump material, or chips of wood charcoal, or lumps of paste prepared from sawdust, and then grinding the activated product.

Activated carbon is produced by a process consisting of raw material dehydration and carbonization followed by activation. The starting material is dehydrated and carbonized by slowly heating in the absence of air, sometimes using a dehydrating agent such as zinc chloride or phosphoric acid.

Excess water must be removed from the organic material. Carbonization converts this organic material to primary carbon, which is a mixture of ash, tars, amorphous carbon, and crystalling carbon.

Activation is a two phase process requiring burnoff of the tars, plus enlargement of pores in the carbonized material. Burnoff frees the pore openings, increasing the number of pores, and activation enlarges these pore openings. The particle size is generally considered to affect adsorption rate, but not adsorptive capacity. The external surface constitutes a small percentage of the total surface area of an activated carbon particle.

There are several characteristics of activated carbon of importance in evaluating its suitability to wastewater treatment, including: surface area, apparent density, bulk density, effective size, pore volume, ash percentage, and pore size distribution.

The color in wastewater when recycling the wastewater tends to be a problem. The problem is most prevalent when white and colored grades are sequentially manufactured. To cope with the color problem it is a common practice when starting on white grades to use fresh water and run until the water from the cylinder vats on this grade becomes available for use in the hydropulpers. Most mills develop a color compatibility sequence producing white and proceeding to light colored and then to dark colored grades prior to wash-up and repeating the cycle. (3)

In the situation at hand, a papermill makes fine writing grades as well and text and cover grades from a mixture of recycled furnish, virgin pulp, and deinked recycled furnish. Currently the papermill has a primary clarifier which discharges the effluent to sprayers which are used for irrigation purposes. As of now the groundwater from the sprayers contains minimal contaminants regulated by environmental agencies. However, if the water needs to meet certain regulations before the water is discharged to the sprayers a cleaning system, such as activated carbon adsorption, will be considered.

An adsorption isotherm is the relationship, at a given temperature, between the amount of a substance adsorbed and its concentration in the surrounding solution. If a color adsorption isotherm is taken the adsorption isotherm would consist of a curve plotted with residual color in the water as the abscissa, and the color adsorbed per gram of carbon as the ordinate. A reading taken at any point on the isotherm gives the amount of color adsorbed per unit weight of carbon, which is the carbon adsorptive capacity at a particular color concentration and water temperature. An isotherm test can also tell whether or not the desired degree of purification can be attained with the particular activated carbon tested.(2)

EXPERIMENTAL PROCEDURES

Powdered carbon samples were obtained from both Westvaco and the Kalamazoo Water Reclamation Plant. These carbon samples were donated for the thesis project. The paper mill effluent was donated from the papermill.

The mixers, vacuum filters, and glass filter paper (0.45 micron) were all donated from the National Council for Air and Stream Improvement. The laboratory in which this experiment was conducted was NCASI's laboratory.

The color concentration readings were read using a spectrophotometer in the Chemistry Department.

The experiment began with taking varied amounts of both carbons and the effluent (named Black) and mixing them in the mixers (amounts in Table 1a and 1b). Once a known carbon and effluent amount was established for full color removal it is necessary to determine if that amount was the lowest that was capable of color removal.

Percentages of the known amount of both carbons were taken, leaving the effluent amount fixed, (amounts found in Table 2a and 2b) and the absorbencies were found using the spectrophotometer (absorbencies found in Table 2a and 2b).

Once a determined carbon and effluent dosage, along with a dwell time were established six effluent samples were drawn and each of the carbons were added separately. The samples were mixed for a predetermined time. After the dwell time elapsed the samples were filtered through .45 micron filter paper in order to remove the carbon and any other solids in the sample. Once the samples were filtered they were taken to the Chemistry Department and run through the spectrophotometer. (Results in Table 3a and 3b)

The same experiment was run on the Black color with both carbons.

At this point in the experiment it is evident whether or not color removal is effective with both carbons. Once color removal was established an isotherm study was conducted (refer to Background)

Data for plotting isotherms are obtained by treating fixed volumes of the effluent to be tested with a series of known weights of carbon (values found in Table 4). The carbon-liquid mixture is agitated for a fixed time at constant temperature. After the carbon has been removed by vacuum filtration, the residual color in the solution is determined using a spectrophotometer (values found in Table 4). From these measurements, all of the values necessary to plot an isotherm may be Literature Cited

Experimental Design

There are two types of carbon systems available for treating paper mill effluent. The two types of systems are (1) a bed system and (2) a primary clarifier feed system.

The primary clarifier feed system involves feeding the carbon into the primary clarifier and settling it out. Once it is settled out it is considered sludge and will be disposed of using a sludge disposal method, usually landfilled. The equipment necessary to perform with such a method include:

Mild steel bulk silo for carbon storage - 2000 ft^3
4 inch rotary valve at bottom of silo
Air pressure at bottom of cone
45 degree cone
Drop through to small screw conveyer
Small slurry tank with mixer at top
1 lb/gal water feed to mixer
Level indicating transmitter
Metering pump
Sludge disposal cost for 7 o.d. tons/dat (21 wet tons/day)

The costs associated with a primary clarifier feed system for Mill A, based on 2 million gallons of effluent per day include $11,600.00 for the required 8 tons per day carbon feed, the fixed capital cost is $200,000.00, and installation plus capital cost is $400,000.00.

(Bill Leedy from Westvaco)

The column system, based on 2 million gallons of effluent per day, would include:

Virgin carbon - $.80 per lb
2 carbon beds 25 feet long, 11 feet wide, and 14 feet high
Beds require 20,000 lb of carbon each
Bulk changeout

The costs associated with a bed system would be between $120,000.00 and $140,000.00 excluding the freight of carbon. Once the carbon has reached its carrying capacity it will require reactivation. The reactivation process will reduce the activation of the carbon by 10-15%. The supplier, however, will replenish the reactivated carbon with virgin carbon.

Discussion

The first stage in the experiment is to determine the amount of both carbons that will effectively remove the color from the effluent sample. Shown in Table 1a and 1b the Westvaco carbon removed the color when using 125mg/250ml and the KWTP carbon did not effectively remove the color at that dosage. This could be because the Westvaco carbon is designed for color removal whereas the KWTP is designed for organic removal. This concludes that further experimentation needed to be conducted in order to find the dosage of both carbons that will remove the color. The results of absorbency versus carbon dosage can be found in Figure 1 and 2.

Larger amounts of carbon were added to the effluent to yet determine what carbon addition was needed for complete color removal. Table 1a and 1b show that 250mg/250ml was the amount of carbon and effluent that effectively removed the color with each carbon. This concludes that 250mg/250ml is the lowest dosage of carbon that can be added to 250 ml of effluent to effectively remove the color. The results of absorbency versus carbon dosage can be found in Figure 1 and 2.

After the first goal of the experiment, which was to prove and show that carbon can remove color from colored effluent, was concluded each of the carbons were added to six effluent samples of the same size and of the same color to prove with more than one effluent sample that the carbon can remove the color consistently in each of the samples. The data can be found in Table 3a and 3b.

The negative numbers in the data points indicate that the results are so close to zero that they bounce around zero, thus, resulting in negative values.

A sample was obtained from Mill A which was a pinkish color. The experiment was conducted on the effluent with each carbon. The original effluent sample, without any carbon addition, showed after filtration that the color was completely filtered out. After discussion with Mill A it was concluded that the color attached to the fines in the effluent sample and filtered out with the fines. Therefore, the pink color was not a true representative of the effluent characteristics from Mill A and was disregarded as data.

Since the color which much of the experiment was conducted on was Black it was decided that Black was the worst case scenario and would be acceptable to use on the rest of the experiment.

In order to conduct an isotherm study different amounts of carbon needed to be added to the effluent. Westvaco's carbon is designed for color removal, and essentially acted the same as the KWTP carbon except at low dosages, it was chosen for the isotherm study. Since 250 mg/250 ml is the amount of carbon that effectively removed the color percentages of 250 mg were taken; 1, 10, 15, 20, 24, 25, 50, and 75%. the results can be found in Table 4. The isotherm plot can be found in Figure 3.

As stated previously, the isotherm study is used to find the relationship between the amount of color absorbed and the amount of carbon needed to do so. The data found in Table 4 can be used in the design of carbon systems for water treatment. The isotherm plot suggests that any carbon addition above 100 mg/250 ml for the Westvaco carbon will produce complete color removal in the Black color.

Since Black is the worst case scenario it can be suggested that 100 mg/250 ml will remove the color from all other color effluent samples from Mill A. Although it was stated earlier that 250 mg/250 ml was needed for complete color removal, it is important to remember that the 250 mg/250 ml was needed to remove color using both carbons.

The data collected throughout the experiment was useful in determining the second goal of this experiment; which carbon system is more cost effective? The answer is the carbon bed system. Although the amount of equipment needed to use a carbon bed system is greater than that of the primary clarifier addition system the benefit is that the carbon is able to be used over and over after regeneration.

The primary clarifier addition system is costly mainly because the carbon is added to the clarifier and is not collected for regeneration, rather it is disposed of with the sludge. The carbon, therefore, needs to be added often; 8 tons per day.

The carbon bed system is more cost effective since the carbon is added to the two beds and once the carbon reaches the breakthrough point (the color is no longer removed since the carbon has reached its adsorption capacity) the carbon is changed out, regenerated, and then brought back for use.

The bed process is less expensive since the carbon is reused and virgin carbon is not needed except initially and then again at the reactivation time. During the reactivation time the carbon loses 10-15% of its activation and therefore virgin carbon is needed to replenish that amount of loss.

Results

Table 1a

Westvaco

Carbon (mg)	Effluent (ml)	Absorbency (mg/ml)
37.5	250	0.0084
125	250	-0.0051
175	250	-0.0049
250	250	-0.0054
375	250	-0.0049
500	250	-0.0055

Table 1b

Kalamazoo Water Reclamation Plant Carbon

Carbon (mg)	Effluent (ml)	Absorbency (mg/ml)
37.5	250	0.0094
125	250	0.0043
175	250	0.0051
250	250	-0.0010
375	250	-0.0052
500	250	-0.0049

Table 2a

Westvaco

Carbon (mg)	Effluent (ml)	Absorbency (mg/ml)
62.5	250	0.0094
125	250	-0.0051
188	250	-0.0051

Table 2b

Kalamazoo Water Reclamation Plant Carbon

Carbon (mg)	Effluent (ml)	Absorbency (mg/ml)
62.5	250	0.0296
125	250	0.0546
188	250	0.0450

Table 3a

Westvaco

Carbon (mg)	Effluent (ml)	Absorbency (mg/ml)
250	250	0.0006
250	250	0.0027
250	250	-0.0041
250	250	-0.0039
250	250	-0.0010
250	250	-0.0088

Table 3b

Kalamazoo Water Reclamation Plant Carbon

Carbon (mg)	Effluent (ml)	Absorbency (mg/ml)
250	250	0.0101
250	250	-0.0083
250	250	-0.0054
250	250	0.0001
250	250	-0.0019
250	250	-0.0043

Table 4

Westvaco

Carbon (mg)	Effluent (ml)	Absorbency (mg/ml)
0	250	0.1113
2.5	250	0.0890
25	250	0.0344
37.5	250	0.0601
50	250	0.0507
60	250	0.0519
62.5	250	0.0074
125	250	-0.0051
188	250	-0.0051

Conclusion

Powdered activated carbon adsorption was evaluated in this thesis to determine whether or not two separate carbons were able to remove color from a paper mill's effluent. After it was determined whether carbon has the potential to remove color the results were used to develop two types of carbon systems; bed system and primary clarifier carbon addition system. The cost effectiveness of both systems were established and evaluated.

The experiment consisted of adding two separate carbons to colored paper mill effluent and then mixing them constantly for one hour. After the mixing was conducted the samples were filtered using a vacuum filter through a 0.45 micron glass filter paper. The samples were then read through a spectrophotometer to determine the absorbency of the sample.

A preliminary laboratory study showed that a dosage of 250 mg of both the Westvaco carbon and the Kalamazoo Water Treatment Plant's carbon when added to 250 ml of paper mill effluent will remove all of the color. The resulting absorbency for the Westvaco carbon is -0.0054 (mg/ml) and for the KWTP carbon the absorbency is -0.0010 (mg/ml).

To establish the fact that 250mg/250ml was effective for color removal with both carbons, six effluent samples of 250 ml contained additions of 250 mg of carbon and the results proved that in all six samples the color was removed.

Percentages of the 250 mg of the Westvaco carbon were taken, 1, 10, 15, 20, 24, 25, 50, and 75, and added to 250 ml of effluent. The absorbencies were found using the spectrophotometer and used to develop the isotherm plot. The plot showed that the amount of carbon necessary for complete color removal using the Westvaco carbon was 100 mg/250 ml of effluent.

Using the isotherm plot two carbon systems were developed; a bed system and a primary clarifier addition system. The isotherm established how much carbon was needed for each system. Eight tons per day of carbon is needed for the primary clarifier addition system and 40,000 lbs. of carbon is needed for two carbon beds for the bed system.

In evaluating the costs of each system, the bed system turned out to be the most cost effective. Since the carbon is able to be reactivated and reused in the bed system it eliminates carbon costs whereas the primary clarifier addition system requires carbon addition on a daily basis.

It is important to explore other colors and carbons had this been a real mill experiment. Different companies should be looked into and costs should be evaluated in more precise manor.

Recommendations

Based on the data obtained it is evident that the color at Mill A can be removed using powdered activated carbon in the dosages established.

Based on the costs associated with each carbon system stated it is evident that the most economical method of color removal using a carbon system would be the bed system.

However, in serious attempts to establish a best carbon system for a mill there should be further investigations. If one were to use the experiment provided here many more colors should be looked into, not only the darkest one. Also, one might also be more precise in the carbon additions and effluent amounts to find the exact right dosage and not a roundabout value.

When actually considering a carbon system for a mill one should spend time finding the exact values mentioned and then proceeding with a supplier of carbon systems and evaluating them in a trial type fashion. The type of experiment stated in this thesis only establishes the fact that carbon can be removed, and based on the effluent amount of Mill A the costs of two systems can be compared using ball park costs.

Literature Cited

1. Avenell, J.J., Folster, H.G., Sierka, R.A., International Environmental Conference, 1994. "The Treatment of Whitewater by Adsorption". pp. 249-257.

2. Klinker, R.T., Wieland, A., Pollution Prevention Review, Summer 1993. "Case Study: Hennepin Paper's Zero Discharge Program and Wastewater Recyling System". pp. 307-316.

3. NCASI, Technical Bulletin NO. 340. "Laboratory Investigations of the Effectiveness of Two Color Reduction Methods". pp. 6-18.

4. NCASI, Technical Bulletin NO. 557. "Pulp and Paper Mill In-Plant and Closed Cycle Technologies - A Review of Operating Experience, Current Status, and Research Needs". pp. 17-35.

5. Garland, C.F., Beebe, R.L., Water Pollution Control Research Series. "Advanced Wastewater Treatment Using Powdered Activated Carbon [illegible] Clarifiers".

6. Culp, R.L., Culp, G.L., Wesner, G.M., Handbook of Advanced Wastewater Treatment, 2nd Edition., Van Nostrand Reinhold Company., pp. 166-195.

7. Institute of Paper Chemistry, Project 3029, "Continued Study of Advanced Waste Treatment Systems for Combined Municipal and Pulp and Paper Wastes", July 10, 1974.

8. [illegible] TAPPI 57 (4):45-52 (April 1974), "Water Recycling in the Pulp and Paper Industry".