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NOTE

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Abstract

We report the results obtained on lignocellulosic kraft wastewater cleaning by adsorption using the Rohm & Haas polymeric adsorbent Amberlite XAD-7. This resin shows a suitable retention capacity for ligninic compounds, but not for carbohydrates derived from cellulose and hemicelluloses. Regeneration has also been studied. This can be efficiently achieved with 1 *N* NaOH.

INTRODUCTION

Vian and co-workers (*1*) developed a procedure for kraft wastewater cleaning that starts by dividing the total effluent into three main streams according to their basic composition. Wastewater resulting from the final steps of pulp washing and bleaching operations, as well as accidental black liquor overflows from the recovery section, integrate into the lignocellulosic waste stream which is difficult to treat. It carries chemical species derived from lignin as well as cellulose and hemicelluloses hydrolysis, is brown in color, and has significant chemical oxygen demand (COD) and biochemical oxygen demand (BOD) values.

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The treatment method for this particular waste stream consists of an acid coagulation of highly condensed ligninic compounds followed by a carbon adsorption step to remove the colored hemilignins remaining in solution. A final biological treatment for carbohydrates leads to a reusable effluent.

Carbon adsorption is the critical step of the above procedure from an economic point of view (*2, 3*). The cost of this step is mainly determined by the regeneration of exhausted carbon. It is therefore of interest to study the possibility of using more easily regenerable adsorbents that will lead to a more favorable cost.

There is a series of macroreticular resins developed by Rohm & Haas and identified as Amberlite XAD (*4*). These adsorbents have been used in the last 10–15 years in wastewater treatment. Crook et al. (*5*) reported the results obtained on phenols removal from industrial waste effluents with Amberlite XAD-4 and XAD-7. Another dephenolization study using Amberlite XAD-4 is given in Ref. *6*. Decolorization of kraft pulp bleaching effluents using Amberlite XAD-8 has been investigated by Rohm & Haas (*7*).

In this paper we present a study of the possibilities of using Amberlite XAD-7 as a substitute for activated carbon in the adsorption step which follows the acid coagulation treatment of kraft lignocellulosic effluents.

EXPERIMENTAL

The adsorption runs were carried out in a 3-cm diameter glass column using a downflow configuration. A sand filter was placed before the column. Effluent samples from the column were collected and analyzed for color and COD. Color was determined according to the Pt-Co method, using a Bausch & Lomb Spectronic 700 spectrophotometer for absorbance measurements and operating at 465 nm wavelength as described in Ref. 2. The pH of the samples was always adjusted to 7 to avoid any error derived from color variations of ligninic compounds with pH. The dicromate reflux method (*8*) was used for COD.

Regeneration work was also performed in a 3-cm diameter column. In this case the eluate was analyzed for COD. In each run the total COD retained by the bed in the adsorption stage was determined.

Simulated wastewaters were prepared from black liquors obtained in a 2-L stainless steel laboratory digester by cooking *Pinus Sylvestris* chips with a $NaOH-NaS_2$ solution (68.6 g/L active alcali and 25.5% sulfide) at 7–7.5 kg/cm^2 pressure with a digestion time of 2.5 h and a liquor-to-wood ratio of 5:1. The black liquor was diluted to 2% with distilled water, and

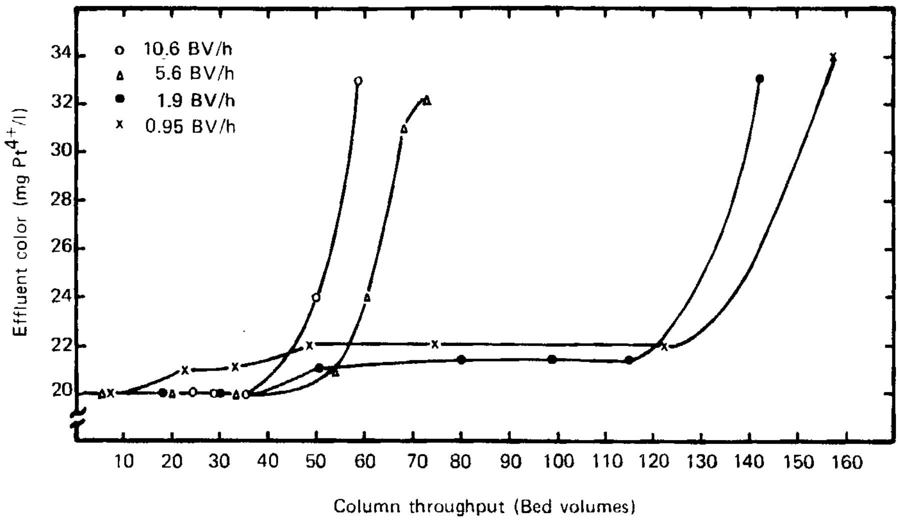

FIG. 1. Breakthrough curves for color removal.

the resulting product was treated with concentrated H_2SO_4 until pH = 4. The flocs formed were separated by settling, and the clarified liquid was passed through filter paper to obtain the feed wastewater for the adsorption runs.

The Amberlite XAD-7 resin was sieved, and the fraction with particle sizes between 297 and 840 μm was collected for the adsorption runs. This was repeatedly washed with methanol and water prior to use.

The following are the most important properties of Amberlite XAD-7 adsorbent (*9*):

Chemical nature	Acrylic ester
Porosity volume	55%
Surface area	450 g/cm^3
Average pore diameter	80 Å
Pore diameter range	30–1800 Å
Skeletal density	1.24 g/cm^3

RESULTS AND DISCUSSION

Figure 1 shows the breakthrough curves obtained for color removal. The initial color of the experimental wastewaters was 152–154 mg Pt^{4+}/L. As can be seen, a color leakage lower than 20 mg Pt^{4+}/L was not obtained. Nevertheless, the adsorbent shows very good performance at this level.

TABLE 1
Leakage COD Values

Flow rate (BV/h)	Initial COD (mg/L)	Leakage COD (mg/L)
0.95	1165	603
1.90	907	620
5.60	1100	750
10.60	930	660

Even at a flow rate as high as 10.6 bed volumes (BV)/h, a treatment capacity of 35 BV is obtained at the breakthrough point. This capacity reaches a value of 125 BV at the lower flow rate tested. These results show the ability of Amberlite XAD-7 to retain most of the colored ligninic compounds which remain in solution after the acid coagulation step. The leakage color may correspond to components with a larger molecular size which cannot penetrate into the pores or which would require a longer contact time than we used.

With the results from Fig. 1, the following relationship has been obtained between contact time and breakthrough time:

$$t_b = 2.23t_c - 9.35$$

where t_b is the breakthrough time in hours and t_c is the contact time in minutes.

From this equation a critical value of 4.2 min is obtained for the contact time.

With respect to COD, the adsorbent showed a markedly lower efficiency. Table 1 shows the leakage COD values obtained at different flow rates.

In previous work (*10, 11*), by means of UV analyses, we concluded that Amberlite XAD-7 adsorbent mainly retains the ligninic compounds present in these wastewaters. The high leakage values obtained for COD may be due to carbohydrates derived from cellulose and hemicelluloses. To confirm this point, we treated a sample of wastewater with activated carbon which removes the dissolved ligninic matter but not the carbohydrates (*12*). The resulting solution had a COD of 776 mg/L. This was brought into contact with Amberlite XAD-7 (4 g/L dose). The COD decreased only 10 mg/L, to a final value of 766 mg/L. Amberlite XAD-7 seems to be a very poor adsorbent for the carbohydrates present in these wastewaters.

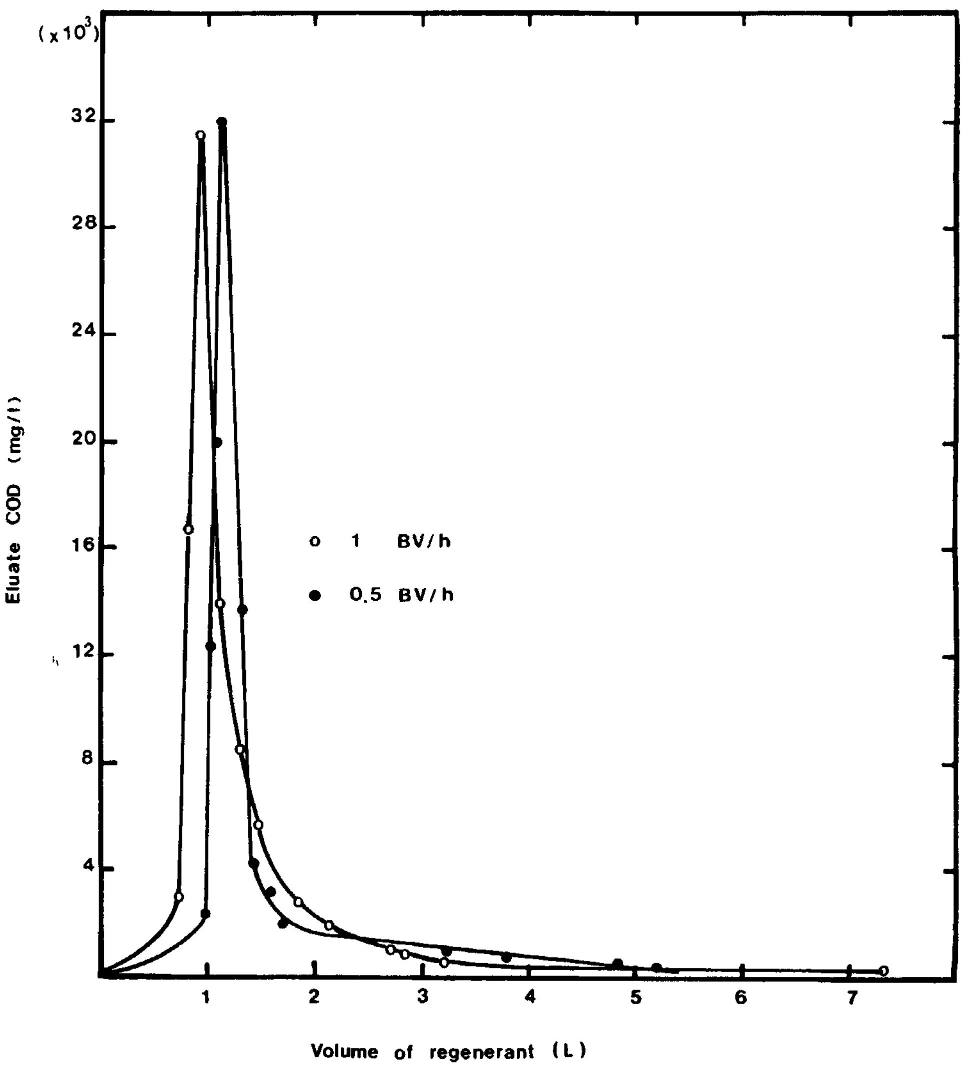

FIG. 2. Regeneration curves of Amberlite XAD-7 with 1 *N* NaOH.

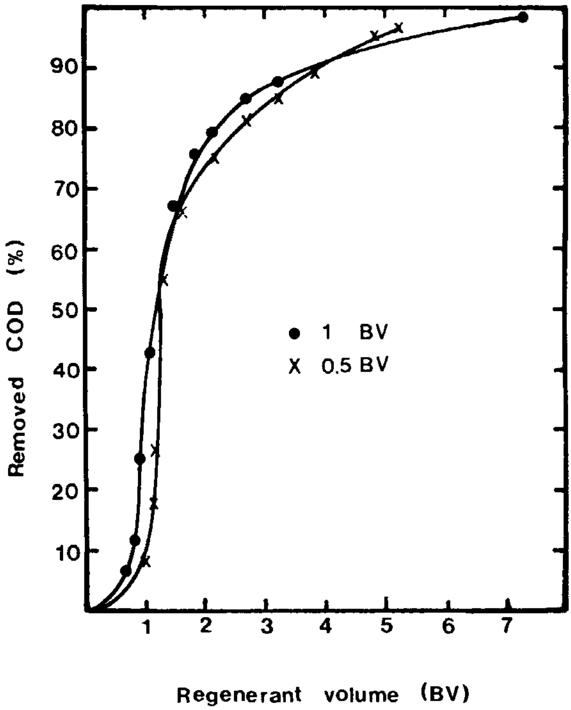

FIG. 3. Regeneration of Amberlite XAD-7 with 1 N NaOH.

Regeneration research was carried out in the same column described for adsorption. Wastewater was passed and the effluent was analyzed for COD. The total COD retained by the bed was calculated by determining the area over the breakthrough curve COD $= f(V)$. Then the regenerant was passed through the exhausted bed and the COD of the eluate was determined. The area under the elution curve gives the COD removed from the bed, which can be calculated for different volumes of regenerant and expressed as a percentage of the total COD retained in the adsorption step. The same flow rate was used in each experiment for adsorption and regeneration.

A previously run set of experiments were used to select the regenerant. Ethanol, acetone, and NaOH solutions of different concentrations were checked. A 1-N NaOH solution was selected as the most adequate regenerant.

Figure 2 shows the regeneration curves obtained with 1 N NaOH at two different flow rates. From these curves we derived the ones shown in Fig.

3. Ninety-five percent regeneration can be obtained with five bed volumes of 1 *N* NaOH at the flow rates used.

ECONOMICS

Amberlite XAD-7 is a more economic adsorbent than activated carbon for treating the lignocellulosic kraft effluents described. It is estimated that for a 100 T/d pulp mill (*10*), the cost of the adsorption step can be reduced to 55 ¢/m^3 of lignocellulosic wastewaters, which represents a reduction of 5.5¢/m^3 referred to the total mill's effluent. Assuming 100 m^3/T of pulp, the cost reduction would be $5.5/T of pulp.

The use of 1 *N* NaOH as the regenerant with Amberlite XAD-7 fits perfectly into the pulp-making process because the eluate from the regeneration step can be used to prepare the pulping solution. The volume of regenerant required to achieve 95% regeneration is less than 20% of the white liquor used for wood coking, and the NaOH concentration of the latter system is in general higher than 1 *N*. Moreover, the presence of organics, mainly ligninic compounds, in the 1 *N* NaOH solution after regeneration creates no problem because of their low concentration, which would not exceed 2500 mg COD/L referred to the total volume of regenerant used. This represents a value of about 500 mg/L for the white liquor.

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