Macromol. Symp. ***155****, 171–180 (2000)*

Adsorbent Usage for VOC Removal in Synthetic Latices

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SUMMARY: In the synthetic latex industry, there is a trend towards lower VOC levels. This paper describes an alternative to the current steam stripping or chemicals injection processes, namely using adsorbents for VOC removal for a styrene-butadiene latex. Both batch and continuous adsorption experiments were performed to screen adsorbents, experimental conditions and simulate plant scale-up. The removal effect of the adsorbents was determined using gas chromatography (GC). It was found that activated carbon had the best VOC removal efficiency, and optimum operating conditions existed at a pH of 10.5, and ambient temperature. It was further found in the carbon bed experiments that the VOC level could be lowered down to 150 ppm, which was the minimum attainable. The regeneration of the spent carbon using solvent extraction was also investigated. Several solvents were tested, and toluene was found to be the most efficient.

Introduction

The removal of volatile organic compounds (VOC) from latices is a major concern for latex manufacturers. VOC's include unreacted monomers, reaction byproducts and raw material impurities. Unreacted monomers can be oligomerized using redox systems, and steam stripping removes both reactive and non-reactive VOC's. The following paper describes a novel approach to VOC reduction, the use of adsorbents. This has been documented previously for VOC reduction in acrylic polymers[1]. Two important experimental constraints were found. In order for the adsorption process to be effective, the adsorption temperature had to be above the Tg (glass transition temperature) of the latex, and the presence of residual oxidizing agents reduced the effectiveness of the activated carbon.

The present work extends the use of adsorbents for VOC removal to fatty acid-KOH based styrene-butadiene latex with a Tg below room temperature, and a low residual oxidant level. Different adsorbents and conditions were tested in batch experiments to analyze their efficiency and optimum operating conditions. Experiments determining the potential for scale-up were performed in a lab sized continuous packed column. To

CCC 1022-1360/00/$ 17.50+.50/0

dispose of spent carbon can be costly, and solvent regeneration is proposed as the regeneration technique.

Experimental

The adsorbents were supplied by Calgon Carbon Corporation (powder and granular activated carbon, granular activated carbon used unless indicated), Grace Davidson (aluminosilicate zeolite, Sylosiv A10) and Dow (polymeric adsorbent Dowex L493). To a bottle containing between 0.5 - 9.0 gr. of adsorbent, 100 grams of latex were added, and then the bottle was put on a shaker for 48 hours. The activated carbon was filtered off, and the VOC levels were analyzed using a capillary column gas chromatograph (GC) with a flame ionization detector (FID) and high purity helium as the carrier gas.

A packed column setup consisting of either 2 or 4 columns (diameter = 0.05 m, height = 1.2 m, void volume/column = 1.4 liters) filled with granular activated carbon was constructed. The columns were connected using 1.25 cm diameter tygon tubing. A pump was placed in front of the columns, and used to push candidate latices through the columns. The latex was bottom fed to each column. The feed rate was varied from 120-180 ml/min. The latex solids content was measured using a CEM Microwave analyzer and the surface tension was measured using a tensiometer.

For the solvent regeneration experiments, the solvents tested (acetone, methanol, toluene) were added to small vials containing spent activated carbon from the continuous column trials. The vials were put on a shaker for 48 hrs. The previously mentioned GC setup was used to analyze the solvents, while a capillary column gas chromatograph (GC) with a thermal desorption unit and high purity helium as the carrier gas was used for the analysis of the activated carbon.

Results and Discussion

In the bottle experiments zeolites, activated carbon, and polymeric type adsorbents were tested and the results are shown in Table 1. The initial volatiles level in the latex was 430 ppm and the addition of 2 grams of activated carbon reduced the level to 324 ppm.

Adding the zeolite decreased the level when 2 grams were added, yielding the same result as activated carbon. The result of adding polymeric adsorbent was an increase in the volatiles level. From these results it was determined that activated carbon should be used, since it not only performs well, but is more cost effective than zeolite.

Table 1. Effect of 3 adsorbents on VOC levels. (Control=430 ppm)

Adsorbent	Weight (gr)	pH	VOC (ppm)
Zeolite	0.5	10.5	441
Zeolite	1	10.5	440
Zeolite	1.5	10.5	405
Zeolite	2	10.5	336
A.C.	2	10.5	324
P.A	0.5	10.5	687
P.A	1	10.5	538
P.A	1.5	10.5	505
P.A	2	10.5	574

An adsorption isotherm was developed for the latex - activated carbon system. It is applied to determine the feasibility of using activated carbon during certain conditions, and to provide guidance for the amount of activated carbon needed to completely remove the impurities in the liquid phase when used in a packed column setup. It also shows the distribution of impurities between the adsorbed phase and the bulk latex. The isotherm can be determined using the empirical Freundlich isotherm equation, eq'n 1[2]. X/M is the

$$\frac{X}{M} = kC^{1/n} \qquad \text{(eq'n 1)}$$

amount of impurity adsorbed per unit weight carbon, C the equilibrium concentration after adsorption, and k and n are constants. Linearizing equation 1 it becomes:

$$\log(\frac{X}{M}) = \log k + \frac{1}{n}\log C \qquad \text{(eq'n 2)}$$

X/M is then plotted vs. C on log scale, and k and 1/n can be solved for. Figure 1 shows the adsorption isotherm developed for our system. The theoretical amount of granular activated carbon needed for maximum volatiles removal in a column setup can be determined by drawing a vertical line from C_o until it meets the isotherm line and then drawing a horizontal line across to read off the corresponding X/M value. In our case, with C_o equal to 750 mg/l, X/M was equal to be 45 milligrams impurity per gram activated carbon, which represents 17 grams activated carbon for complete volatiles removal per one liter latex using a column setup. Complete volatiles removal in a latex using activated carbon is however not possible, as will be discussed.

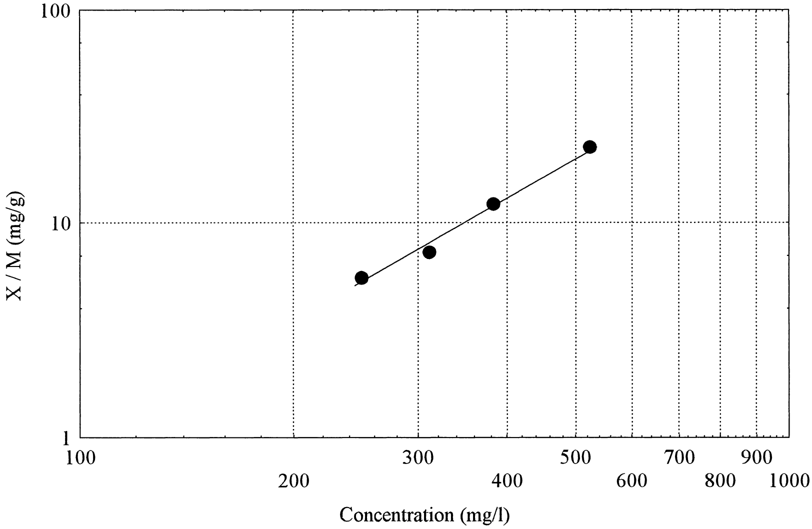

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Fig. 1: Adsorption isotherm for latex using granular activated carbon.

The type of latex analyzed is pH sensitive due to the stabilization system used and therefore the effect of the pH was investigated. These results are shown in Table 2. The effect of temperature is shown in Table 3. It was desired to use the latex at its preferred pH of 10.5 and at ambient temperatures, and both sets of results indicate that there is no advantage to change either. Accordingly, during the packed column experiments, the latex could be used as received and at room temperature. Table 3 also indicates that the removal percentage efficiency is maximized for 1 gr. of activated carbon at both 25 and 50° C. This may be explained by the makeup of the VOC impurities. Some impurities are more hydrophilic with lower partition coefficients than more hydrophobic impurities and they diffuse more readily into the water phase where they can be adsorbed onto the activated carbon. A certain amount of activated carbon is sufficient to remove the hydrophilic impurities. The polymer particle exit frequency for the more hydrophobic impurities is lower, so the probability that they will adsorb onto a carbon particle is lower and thus the removal rate is lower. To counteract this effect, more carbon is required. This then lowers the removal efficiency per gram carbon.

Table 2. Effect of pH on VOC levels. (Control = 430 ppm)

Adsorbent	Weight (gr)	pH	VOC (ppm)
A.C.	2	10.5	324
A.C.	2	11	409
A.C.	2	12	408
A.C.	2	13	332

Table 3. VOC levels (ppm) in latex: effect of temperature and activated carbon amount (pH 10.5).

Temp. (C)	A.C. (gr)	VOC in (ppm)	VOC out (ppm)	% removed/ gr adsorbent
50	0.5	687	675	3.5
50	1	687	400	41.8
50	1.5	687	336	34.1
50	2	687	340	25.3
25	1	475	275	42.1
25	3	475	120	24.9

Table 4 shows the major VOC impurity levels before and after the addition of activated carbon. It clearly indicates the removal capability of activated carbon and that some impurities are easier to remove than others.

Table 4. VOC levels (ppm) in latex; before and after addition of powder activated carbon (pH 10.5, Temperature 25°).

GC Elution time (min)	VOC before (ppm)	VOC after (ppm)	% Removed
1.75	32	11	65
2.5	11	9	18
4.2	12	2	82
5.3	74	1	98
6.5	25	5	81
7	197	67	66
7.5	10	3	69
9	98	25	75

Before the carbon was added to the packed carbon columns, it was soaked for 24 hours with water to displace the gases inside the pores. This water would dilute the first part of the candidate latex pumped through. Therefore, to allow the system to stabilize, samples from the first 4 residual times were not used in the analysis. At the outlet of the fourth column, a steady-state VOC level of approximately 150 ppm can be observed between 2-4 hrs if the column is continuously run at 120 ml/min. This is seen in Figure 2 between residence times 10-25. There was no complete VOC removal using the carbon columns, indicating a very long mass transfer zone and a very short breakthrough time. The challenge is that the latex - activated carbon system investigated is a three-phase system. The volatiles first have to exit the polymer particles, diffuse through the liquid phase, and then enter the activated carbon particles. As less hydrophilic molecules remain in the polymer particles, their partition coefficients increase with respect to the polymer particles, making it harder for them to exit the polymer particles. This means that eventually an equilibrium is reached beyond which the latex volatile level will not decrease substantially unless there is a facilitating driving force. This also applies to the Freundlich isotherm which does not hold true at lower volatile levels. Further supporting evidence for this was found during the bottle experiments, shown in Table 4, and discussed in the previous section.

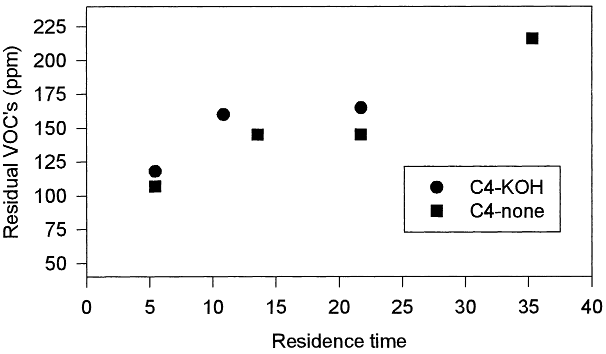

Fig. 2: VOC levels for KOH treated and non treated carbon columns (data taken at fourth column outlet, control = 600 ppm)

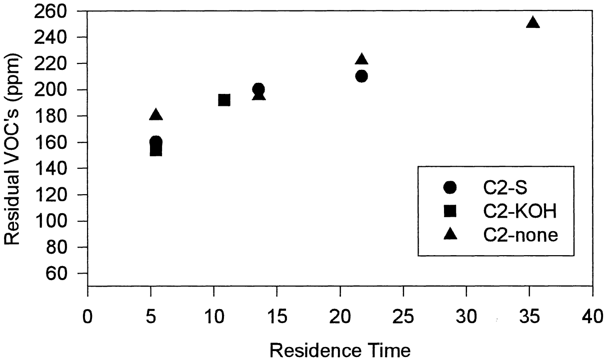

Fig. 3: VOC levels for KOH and surfactant (S) treated and non treated carbon columns (data taken at second column outlet, control = 600 ppm)

Attempts were made to lower the steady state level by pre-treating the column with potassium hydroxide and a surfactant solution. The pre- treatment experiment using the surfactant solution was only performed using a 2 column setup due to the high viscosity of the surfactant solutions. The results are shown in Figures 2 and 3. The only other difference between the runs was that the non treated experiment had a slightly lower feed rate. When investigating the figures, there is no difference in the outlet VOC levels between the different pre-treatments. It can be concluded that pre-treating the carbon did not have a significant effect. Instead, it is seen in Figure 3 that the outlet VOC level is slowly increasing almost linearly during the 3 experiments. This indicates that the activated carbon is getting saturated.

Product changes did occur during the column trials. Most notably the solids content decreased (~1%), and the surface tension increased, indicating adsorption of both polymer and surfactant onto the carbon particles. It represents a few percent product loss, which would not be desired in the long run.

Table 5. VOC levels in toluene after adding it to spent carbon

Carbon:Toluene	VOC (ppm)
1 : 3	2750
1 : 10	1540
1 : 30	1160
pure toluene	1066

Table 6. VOC levels in A.C. before and after toluene treatment

Condition	VOC (ppm)
Spent A.C.	4741
Regenerated A.C.	1541

A.C. = Activated Carbon

Once the carbon in the column has been saturated it either has to be replaced or regenerated. There are several different ways to regenerate the spent carbon[3]. The list includes thermal, steam and solvent regeneration among others. We chose to focus on solvent regeneration due to cost. Solvent regeneration extracts the impurities in the activated carbon with a suitably selected solvent[4]. The impurities are desorbed into the solvent. The activated carbon becomes saturated with the extraction solvent, which can be easily removed by steam stripping if its boiling point is less than 120°C. The extraction solvent can then be purified using either distillation or extraction. Acetone, methanol and toluene were evaluated as extraction solvents; only toluene effectively desorbed VOC's from the carbon substrate. Table 5 displays the VOC level in the toluene after having added it in different ratios to spent carbon, while Table 6 displays the VOC level in spent carbon before and after the toluene addition. The toluene used was not a high purity grade, so the VOC level shown for the toluene was the existing impurities.

As is indicated in tables 5 and 6, toluene extraction seems to be a feasible approach to activated carbon regeneration. A process for plant scale operation is suggested as follows:

1. Run latex through carbon until carbon is spent.
2. Wash column with solvent. Exiting solvent is pumped to a distillation or extraction column, where the impurities are removed from the solvent. The distilled solvent is then transferred to a storage tank for reusage.
3. The column is then steam stripped. The steam removes the solvent that remains with the activated carbon. The exiting stream is condensed, cooled, and decanted or otherwise separated from the solvent.
4. The column is flooded with water, and the process repeats at 1.

Conclusion

This article has shown the feasibility of using adsorbents, especially activated carbon, to reduce the VOC levels in a styrene-butadiene latex. The feasibility was demonstrated both in batch and packed column experiments. A latex pH of 10.5, room temperature and activated carbon were found to give the best adsorption conditions for the process. Both the batch and continuous experiments indicated significant VOC reductions. The continuous experiments provided a constant VOC removal down to 150 ppm, which held for about 10 residence times. This was found to be the lower limit due to the make up of the system. It is a three phase system, where the volatiles have to exit the polymer particles, diffuse through the water phase, and adsorb onto the activated carbon substrate. A certain lower VOC concentration will be reached where the partition coefficient for the volatiles retards their exiting of the polymer particles, effectively lowering the removal rate. To regenerate the carbon, solvent extraction is a viable candidate. The solvent found to work most efficiently was toluene.

References

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