ADSORPTION OF NITROGENOUS-TYPE COMPOUNDS FROM
SYNTHETIC CRUDE FRACTIONS ON VARIOUS SORBENTS

PIERRE D. CHANTAL, SYED M. AHMED, GILLES JEAN and HENRY SAWATZKY

AUGUST 1986

ERP / ERL . 86-12 (OPJ)

ADSORPTION OF NITROGENOUS-TYPE COMPOUNDS FROM SYNTHETIC CRUDE FRACTIONS ON VARIOUS SORBENTS

by

Pierre D. Chantal, Syed M. Ahmed, Gilles Jean and Henry Sawatzky

Energy Research Laboratories, CANMET, Energy, Mines
and Resources Canada, Ottawa, Canada K1A 0G1

ABSTRACT

The selective adsorption of nitrogenous components from synthetic crude can lead to significant benefits since it will reduce the severity of upgrading treatment dictated by those components. Recent studies have shown that zeolites can selectively adsorb nitrogenous compounds. This paper compares the adsorption capacity of nitrogenous model compounds on different sorbents some of which can be used in analytical separation and some as catalysts or catalyst supports. The basicity of the compounds and the nature of the sorbent influence the adsorption capacity. Based on these data methods for treating synthetic crude naphthas can be developed.

Titre

par

Pierre D. Chantal, Syed M. Ahmed, Gilles Jean et Henry Sawatzky

RÉSUMÉ

La séparation selective par adsorption des composés azotés des bruts synthétiques peut être économiquement viable puisqu'il réduit la sévérité des conditions opératoires de valorisation. Des travaux récents ont montré que certaines zéolithes peuvent adsorber selectivement ces composés azotés. La présente étude a pour but de comparer différents adsorbants utilisés pour les séparations analytiques ou encore comme support de catalyseurs métalliques. Il a été trouvé que la basicité du composé de même que le sorbent lui-même influence la capacité d'adsorption. Ces résultats pourront servir de données de base pour le développement de procédé de valorisation de naphtes synthétiques.

INTRODUCTION

Synthetic crude fractions derived from bitumens, heavy oils, residuals and coals have higher contents of heteroatomic compounds than conventional crude fractions. These compounds are problematic during upgrading and utilization. In commercial operations they are converted by costly hydroprocessing. The objective of this work is to investigate the possibility of separating these compounds as alternatives or aids to hydroprocessing. Such separations could have significant advantages.

To date this work has emphasized the removal of nitrogenous compounds because they dictate processing severities. However, with the limited study of oxygenous compounds it appears that they would be removed with the nitrogenous compounds. Work on sulphur compounds also has been very limited, but if nitrogenous compounds were removed then hydrodesulphurization would be significantly enhanced.

Over the past few years many processes have been developed to remove nitrogenous components from different crude fractions. Different sorbents such as ferric chloride (1,2), macroreticular ion exchange resins (3-4), alumina (5-7), modified silica gel (8) as well as zeolites 13-X (9,10) have been used to adsorb selectively nitrogenous components.

The selectivity as well as the competition for the adsorption sites depend on the sorbent as well as the nature of the compounds. This information is helpful in selecting the best adsorbent or sorbent blends for specific feed to the process.

This paper compares different inorganic sorbents which are usually used in analytical separation as well as in industrial processes. The adsorption capacity has been established using a complex solution of model compounds.

EXPERIMENTAL

A schematic of a computerized laboratory scale adsorption unit developed for this study is presented in Fig. 1. The frequency of sampling, volume of the vial and length of the run can be controlled through a BASIC program written for an APPLE computer.

A typical run consists of pumping an upflow feed continuously at 0.5 mL/min into a 15.0 cm long x 0.94 cm ID stainless steel column. All experiments were performed at room temperature. The pressure measured at the outlet of the pump corresponds to the pressure drop through the column (usually less than 4 MPa).

The feed solution is prepared using 10 model components having higher than 97% purity using toluene as solvent. The composition of the standard feed is given in Table 1. This solution contains weak, strong and non-basic nitrogenous components.

The sorbents were pretreated between 150°C and 450°C under static air (Table 2). The samples were analyzed using a Varian 6000 gas chromatograph equipped with a 30-m long DB-5 capillary column and a FID detector.

Table 1: Composition of the standard feed solution

	Concentration (ppm)	Basicity
Ethyl-pyridine -4	6000	Strong
Aniline	3000	Weak
Benzylamine	1000	Strong
Octylamine	1000	Weak
Indoline	500	Weak
Quinoline	4000	Weak
Indole	2000	Neutral
Phenyl-pyridine -2	500	Weak
Phenethyl-piperidine -1	500	Strong
Dibenzylamine	1500	Strong

RESULTS AND DISCUSSION

The total adsorption capacity of nitrogenous components for different aluminas is presented in Fig. 2. The adsorption capacity is defined as the ratio of the weight of nitrogenous components adsorbed to the weight of sorbent expressed as a percentage. These results show clearly that the adsorption capacity is not affected by the temperature of activation. Little significant difference is observed between neutral, basic and acid aluminas. The highest adsorption capacity is observed for untreated activated alumina at 250°C.

Figure 3 shows the adsorption capacity for activated charcoal, for which the adsorption is strongly dependent on the temperature. The capacity reaches a maximum at 250°C then diminishes at higher temperatures when the charcoal is reduced to ash.

Figure 3 also compares silica gel with silica alumina. These are not affected by activation temperatures between 150°C and 350°C although a slight decrease in the capacity is observed at higher temperatures. These two sorbents give the highest adsorption capacity among the sorbents studied. Figure 4 shows the sorption capacity for zeolite 13X in 1/16" pellet form. There is a slight decrease with increasing temperature. Figure 4 also shows the adsorption capacity for zeolite 13X in powder form for a single component

Table 2: Description of the sorbents

Sorbent	Company
Acidic alumina (80-200 mesh) Activity 1 pH = 4.24	Fisher
Basic alumina (powder) Super 1 grade activity	M. Woelm.Eschwege (Waters)
Neutral alumina (80-200 mesh) Activity 1	Fisher
Activated alumina (80-200 mesh) Type F-20 chromatographic grade	MCB Reagents
Silica gel (28-200 mesh) Dessicant Grade 12	Grace Davison Chemical (Fisher)
Silica alumina (powder) Chromatographic grade	Grace Davison Chemical
Activated charcoal (powder)	Anachemia
13-X-Na (0.5 - 5 µm)	BDH
13-X-Na (Pellets 1/16")	BDH
Kaolin (powder) Laboratory grade	Anachemia

solution of 1.0% quinoline in toluene. In this case the adsorption is higher
than 18% at 250°C. The capacity decreases significantly at higher
temperatures. Further studies are necessary to compare the powder and pellet
forms of zeolite 13-X-Na as well as the cation exchanged zeolite. The capacity
of kaolin powder is also compared in Fig. 4 under the same conditions.

From previous results we have observed that silica gel and silica
alumina show the highest adsorption capacity of model nitrogenous compounds.
However, the total capacity is only one parameter needed to select a sorbent.
Selectivity, adsorption capacity of basic and non-basic nitrogenous components
and the irreversibility of adsorption are other properties of the best sorbent.

Table 3 shows no significant difference in the selectivity of
adsorption between acidic, basic and neutral alumina when activated at 150°C.
At higher temperatures some differences were observed. However, activated
alumina has higher affinity for ethyl-pyridine, aniline, quinoline and indole
compared with the other components. These results explain the higher
adsorption capacity of this sorbent.

Table 4 presents the capacity for each of the three best sorbents
studied. Silica gel and silica alumina have the highest adsorption capacities
at 23.5 and 21.9% by weight respectively. Table 4 also shows the distribution
of activated charcoal in powder form preheated at 250°C. This sorbent has a
strong affinity for benzylamine, octylamine and quinoline. However, it was
observed that most of the components are deadsorbed by compounds having a
stronger affinity for the sorbent.

Table 3: Adsorption capacity of individual components over various alumina sorbents pretreated at 150°C (wt %)

	Acidic	Basic	Neutral	Activated
Ethyl-pyridine -4	1.77	1.69	1.59	3.03
Aniline	1.35	1.46	1.08	1.79
Benzylamine	0.91	1.04	1.03	1.20
Octylamine	0.91	1.04	1.04	1.19
Indoline	0.11	0.10	0.09	0.10
Quinoline	0.54	0.80	0.63	0.96
Indole	0.64	1.03	0.69	1.41
Phenyl-pyridine -2	0.05	0.07	0.05	0.02
Phenethyl-piperidine -1	0.01	0.03	0.02	0.01
Dibenzylamine	0.35	0.24	0.22	0.46
Total	6.64	7.50	6.44	10.17

Table 4: Adsorption capacity of individual components over various sorbents pretreated at 150°C (wt %)

	Silica gel	Silica alumina	Zeolite 13-X-Na	Activated charcoal*
Ethyl-pyridine -4	8.15	7.25	3.76	0.41
Aniline	3.51	2.51	2.80	1.24
Benzylamine	1.62	2.15	1.57	2.83
Octylamine	1.39	2.15	0.94	2.45
Indoline	0.56	0.34	0.24	0.53
Quinoline	5.12	3.32	2.62	1.78
Indole	0.52	1.30	1.03	0.47
Phenyl-pyridine -2	0.53	0.10	0.19	0.21
Phenethyl-piperidine -1	0.52	0.98	0.13	0.07
Dibenzylamine	1.60	1.75	0.59	0.56
Total	23.52	21.85	13.87	10.55

* pretreated at 250°C

The 10 components in the feed solution were chosen to represent a broad range of basicity, molecular structure and boiling point whereas the sorbent was selected to represent different pore distributions and acidity. These results clearly show that the sorption capacity is not only a function of the nature of the compounds but also of the sorbent used.

Table 5 represents the capacity relative to the feed solution for the three best sorbents. The distribution of adsorption capacity of individual components is similar to the feed since the relative capacity is about 1 for each component except indol which is 0.22. Thus silica gel seems to have a very low affinity for neutral nitrogenous components. The capacities are quite different for silica-alumina sorbent. This sorbent seems to have an affinity for strong basic components such as benzylamine, dibenzylamine, phenethylpiperidine-1 and also for octylamine. This sorbent also has a higher sorption capacity for indol compared with silica gel. Zeolite 13-X-Na has a lower capacity compared with silica gel and silica alumina (see Table 4). However, this zeolite has a higher affinity for neutral nitrogenous components such as indol. This last result is very encouraging since these components are the most problematic in hydroprocessing. The lower relative capacity observed with larger molecules such as dibenzylamine, phenyl-pyridine and phenetyl piperidine can be explained by a lower diffusivity in the structure lattice of the zeolite.

Figure 5 shows that the components are irreversibly adsorbed on zeolite 13-X-Na. This information is interesting since it can allow the operation of the adsorption tower in series for industrial applications.

CONCLUSION

This study demonstrated the possibility of using an inorganic solid sorbent to remove selectively nitrogenous components from synthetic crude. The adsorption capacity is not only a function of the basicity of the components, but also of the nature of the sorbent. The preheating treatment did not affect significantly the capacity of the silica gel, silica alumina and activated aluminas. However, the sorption capacity of activated charcoal and zeolite 13-X-Na is highly dependent on such pretreatment.

A process for treating different synthetic crudes can be developed from the previous results. The selection of the best sorbent or sorbent blend will be related to the heteroatom components in a particular feed. Future work should concentrate on identifying the competing heteroatom species and to select the regeneration procedure for those sorbents.

Table 5: Adsorption capacity relative to the feed for individual components for various sorbents

	Components in the feed (%)	Silica gel		Silica alumina		13-X-Na	
		D.C.	C.R.	D.C.	C.R.	D.C.	C.R.
Ethyl-pyridine -4	30	34.7	1.16	33.2	1.11	27.1	0.90
Aniline	15	14.9	0.99	11.5	0.77	20.2	1.35
Benzylamine	5	6.9	1.38	9.8	1.96	11.3	2.26
Octylamine	5	5.9	1.18	9.8	1.96	6.8	1.36
Indoline	2.5	2.4	0.96	1.6	0.64	1.7	0.68
Quinoline	20	21.8	1.09	15.2	0.76	18.9	0.95
Indole	10	2.2	0.22	5.9	0.59	7.4	0.74
Phenyl-pyridine -2	2.5	2.3	0.92	0.46	0.18	1.4	0.56
Phenethyl-piperidine -1	2.5	2.2	0.88	4.5	1.8	0.94	0.38
Dibenzylamine	7.5	6.8	0.91	8.0	1.07	4.3	0.57
	100	100		100		100	

D.C. Distribution of adsorption capacity (%)

C.R. Capacity relative to the feed (D.C. / components in the feed)

REFERENCES

1. Yen, T.F., Shue, F.F., Wu, W.H., Tzeng, D., American Chemical Society, Symposium Series No. 230, 1983, p. 457-466.

2. Choi, H.W., Dines, M.B., Fuel, 64, January 1985, p. 4-8.

3. Prudich, M.E., Cronauer, D.C., Vogel, R.F., Solash, J., Industrial Engineering Chemistry Process Design and Development, 25, 1986, p. 747-756.

4. Sawatzky, H., Ahmed, S.M., George, A.E., Smiley, G.T., Energy Processing/Canada, September-October 1978, p. 65-70.

5. Ford, C.D., Holmes, S.A., Thompson, L.F., Latham, D.R., Analytical Chemistry, 53, 1981, p. 831-836.

6. Holmes, S.A., Thompson, L.F., Fuel, 62, June 1983, p. 709-717.

7. Sawatzky, H., George, A.E., Smiley, G.T., Montgomery, D.S., Fuel, 55, January 1976, p. 16-20.

8. Poirier, M.A., George, A.E., United States Patent 4,529,504, July 16, 1985, 4p.

9. Jean, G., Ahmed, S.M., Sawatzky, H., Separation Science and Technology, 20, 1985, p. 555-564.

10. Jean, G., Bonvie, E., Sawatzky, H., American Chemical Society, Division of Fuel Chemistry, 30 (4), September 1985, p. 474-481.
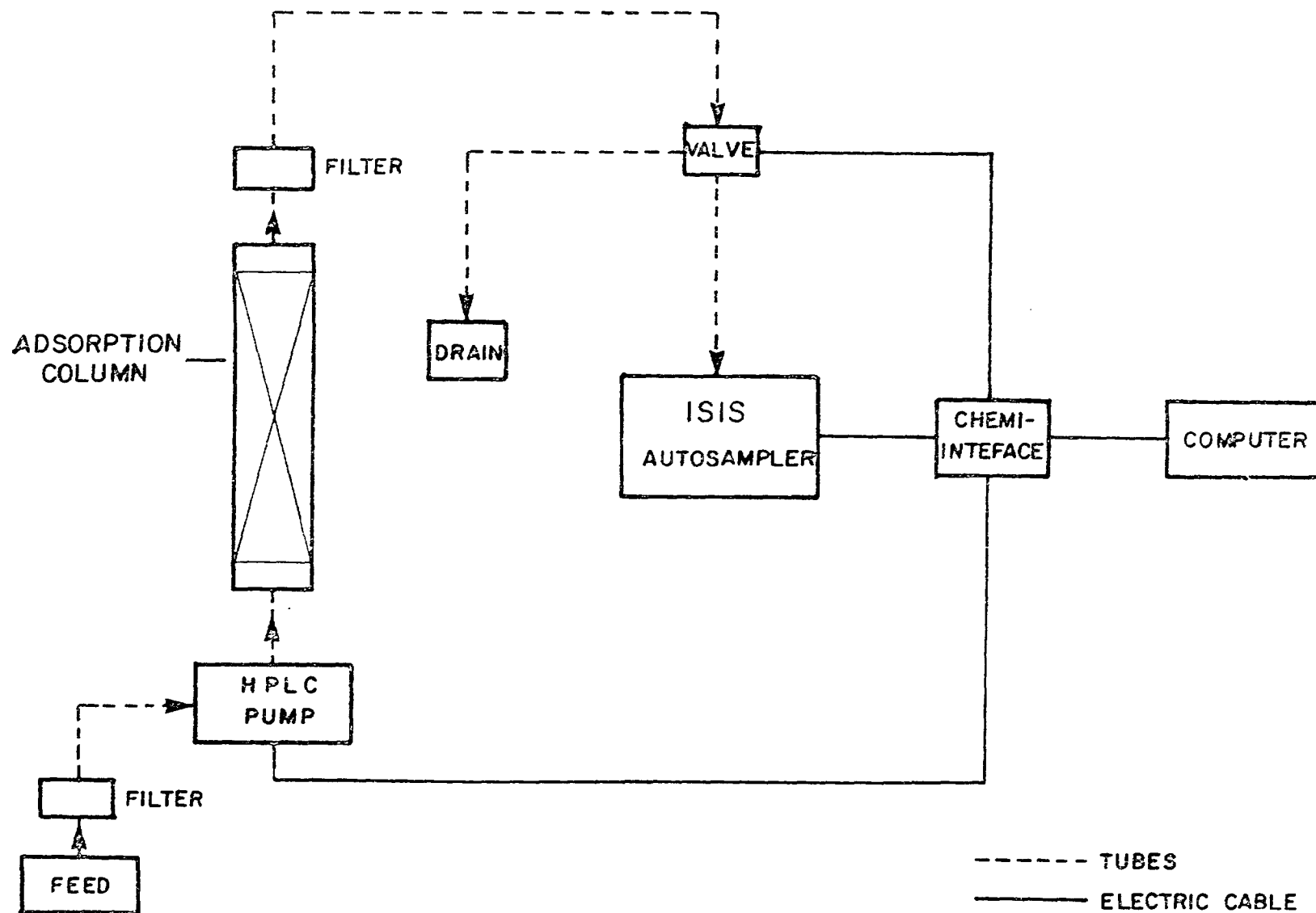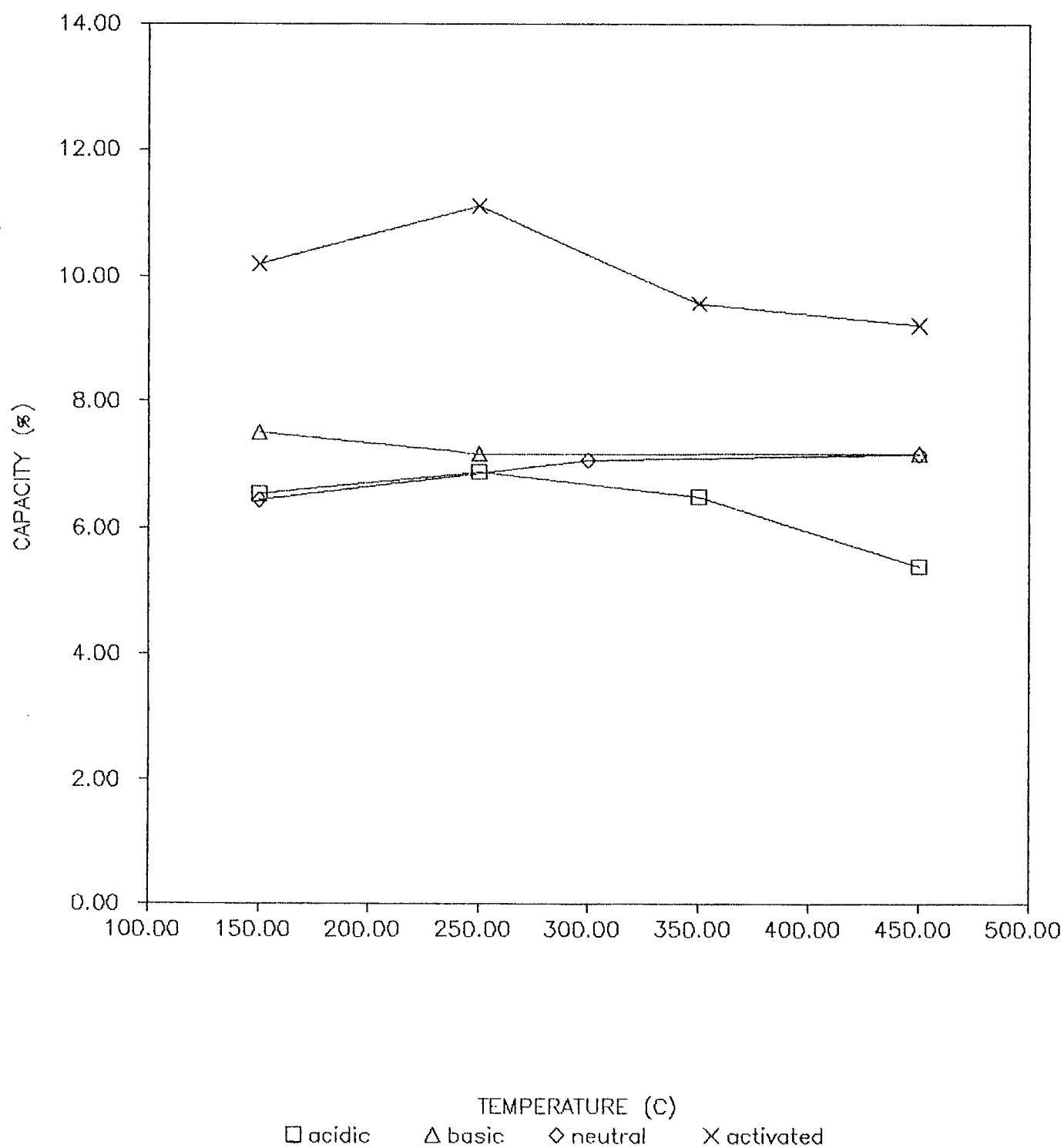
Figure 1: Experimental set-up

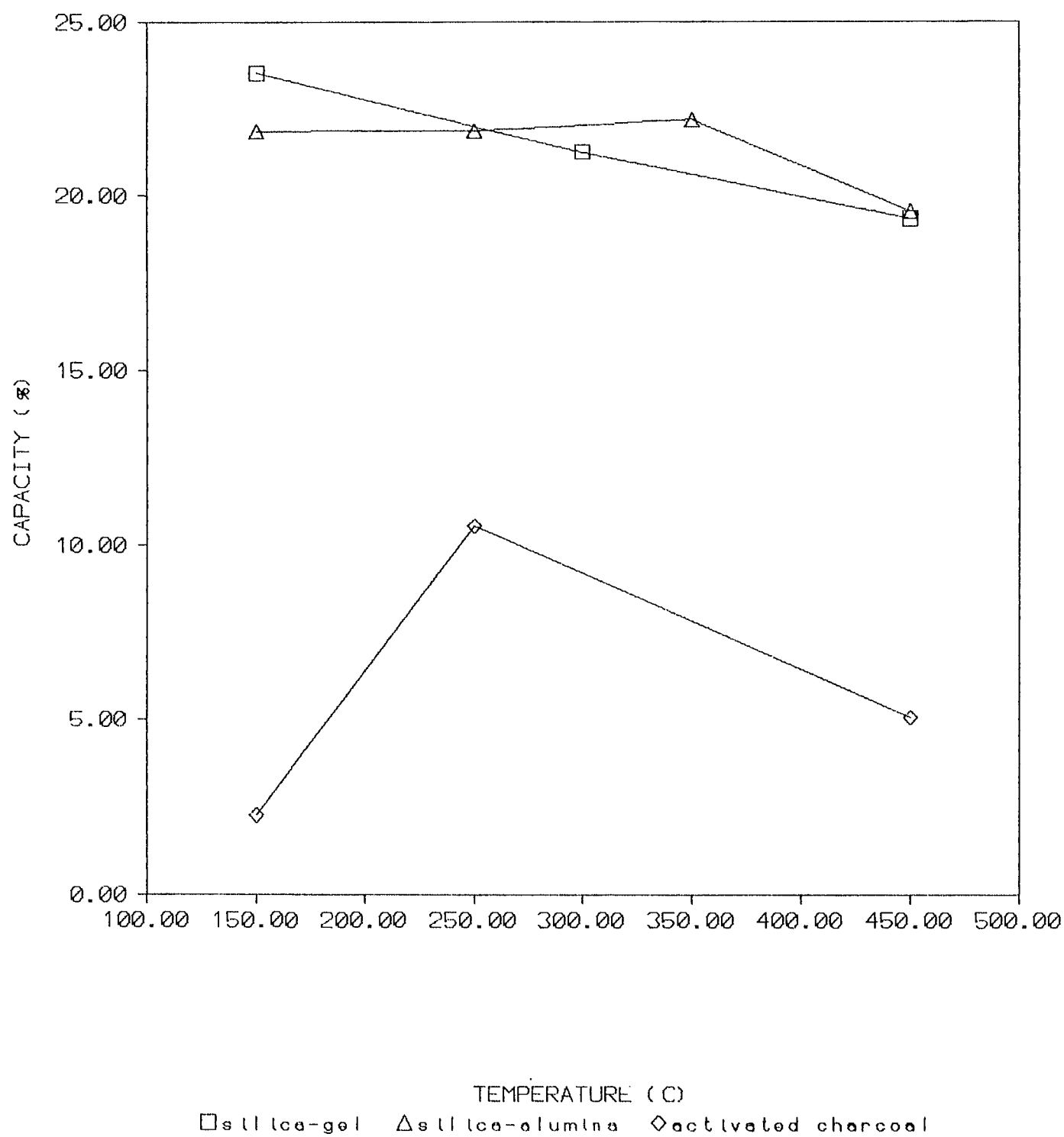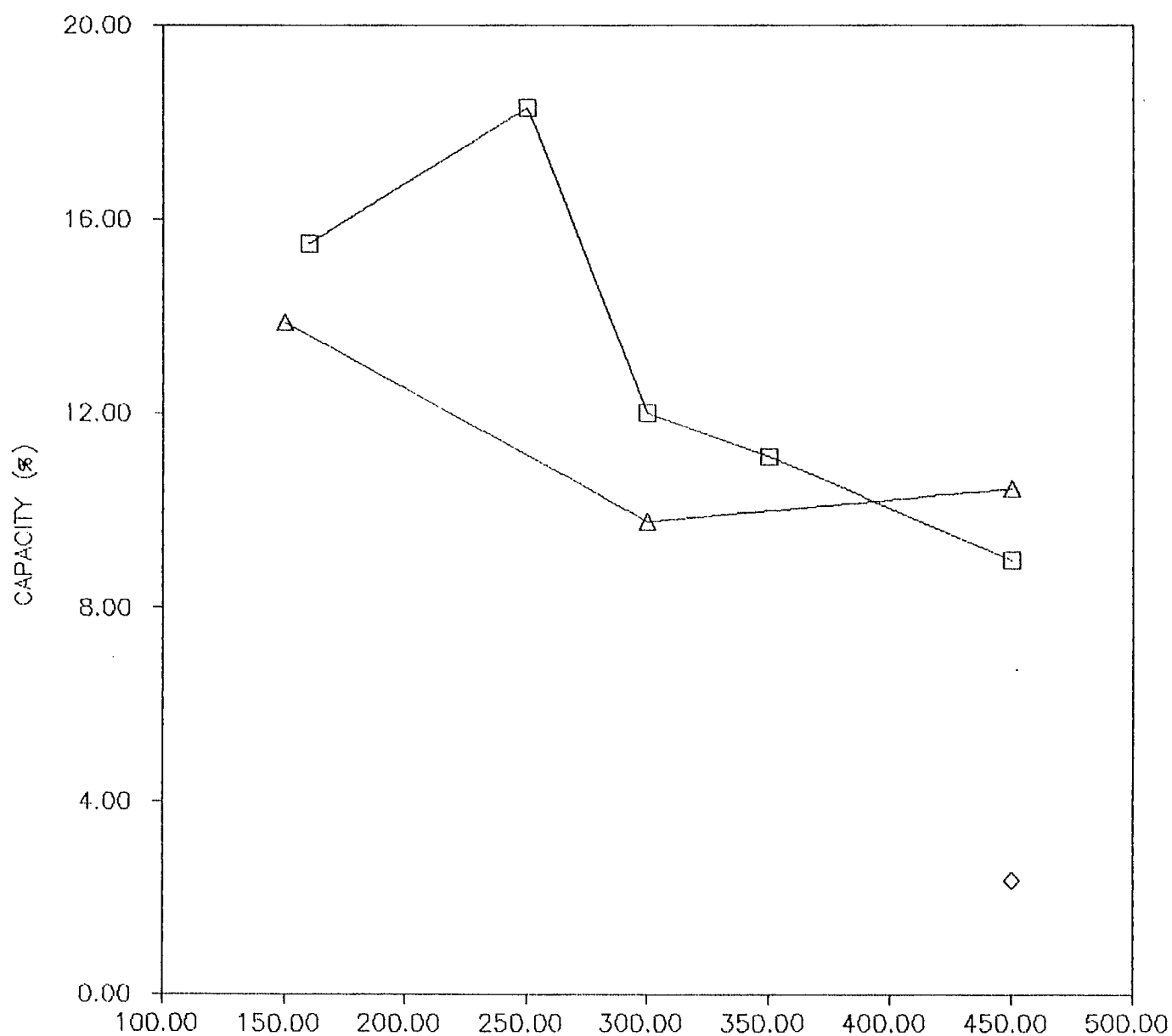Figure 2: Influence of preheating treatment on adsorption
capacity of aluminas

Figure 3:   Influence of preheating treatment on adsorption
            capacity of different sorbents

TEMPERATURE (C)

□ 13—X—Na (powder)   △ 13—X—Na (pellets)   ◇ kaolin powder
    Quinoline(1.0%)   Standard feed   Standard feed

Figure 4:   Variation of adsorption capacity with the temperature
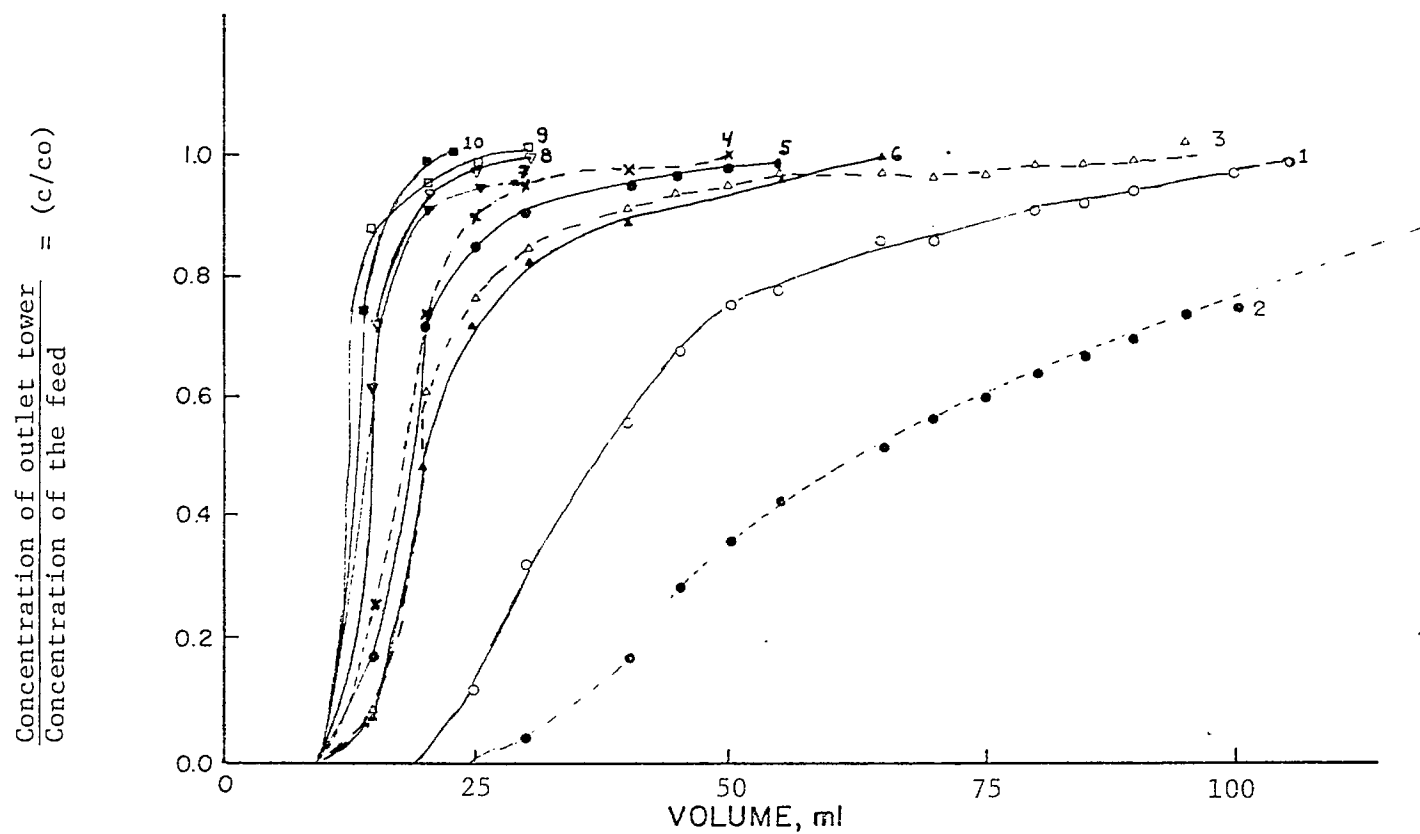   of pretreatment for various zeolites

Figure 5: Breakthrough curves of ten-component mixture of nitrogenous
components over zeolite 13-X-Na

1. aniline
2. benzylamine
3. 4-ethyl pyridine

4. indole
5. indoline
6. quinoline

7. octylamine
8. 2-phenylpyridine
9. 1-phenethylpiperidine

10. dibenzylamine