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ABSTRACT

Several organic impurities formed in the *p*-xylene oxidation process for manufacture of terephthalic acid are carried into the aqueous effluent from the crystallization section of PTA plant of crystallizers for purified terephthalic acid (PTA). These compounds impose a burden on the effluent treatment plant. Due to the presence of these impurities the recycle of aqueous effluent from crystallization section of PTA plant to the PTA crystallizer is not possible. The aim of this study is to check the feasibility of removal of these organic impurities from the aqueous effluent from crystallization section of PTA plant by adsorption on

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polymeric resins so that the aqueous effluent from crystallization section of PTA plant can be recycled resulting in significant saving of process water. Aqueous effluent from crystallization section of PTA plant was characterized and single solute and multisolute adsorption equilibria of the compounds present were determined for a variety of polymeric adsorbents. Column breakthrough study has shown that the components can be removed and recovered from the aqueous effluent from the crystallization section of PTA plant by adsorption.

INTRODUCTION

Terephthalic acid is manufactured by catalytic oxidation of *p*-xylene. A feed mixture of *p*-xylene, acetic acid, and catalyst is continuously fed to the oxidation reactor. The feed mixture also contains water, which is a byproduct of the reaction. The reactor is operated at 175–225°C and 1500–3000 kPa. Compressed air is added to the reactor in excess of stoichiometric requirements to provide measurable oxygen partial pressure and to achieve high *p*-xylene conversion. The reaction is highly exothermic, releasing 2×10^8 Joules per kilograms of *p*-xylene reacted. Water is also produced. Owing to low solubility of terephthalic acid in the solvent, most of it precipitates as it forms. A residence time up to 2 hrs is used. Over 98% of *p*-xylene is reacted and the yield to terephthalic acid is greater than 95 mol%. Due to side reactions or incomplete reaction some impurities are formed and are present in the reactor effluent. The oxidation occurs in steps, with two intermediates, *p*-toluic acid and 4-carboxybenzaldehyde. 4-carboxybenzaldehyde is troublesome, owing to its structural similarity to terephthalic acid. It cocrystallizes with terephthalic acid and becomes trapped and inaccessible for completion of the oxidation. Up to 5000 ppm of 4-carboxybenzaldehyde can be present, and this necessitates a purification step to make terephthalic acid suitable as a feedstock for polyester production. There are also yellow colored impurities and residual amounts of catalyst metals (cobalt, manganese). In the purification step, the crude terephthalic acid is slurried with water and heated until it dissolves entirely. A solution of at least 15 weight percent is obtained and this requires a temperature of ≥260°C. The solution is contacted with hydrogen and a catalyst at high pressure. 4-carboxybenzaldehyde is converted to *p*-toluic acid in the reactor and some colored impurities are hydrogenated to colorless compounds. After reaction the solution passes to a series of

crystallizers where pressure is sequentially decreased. This results in stepped temperature reduction and crystallization of terephthalic acid. The *p*-toluic acid formed in the reactor and other impurities remains in the aqueous effluent from crystallization section of the PTA plant. After the final crystallizer, the slurry undergoes centrifugation, filtration, and drying to give free-flowing terephthalic acid powder as product. Over 98% of terephthalic acid is recovered as a purified product. Water effluent from terephthalic acid process includes water generated during oxidation and water used as purification solvent. This effluent is aerobically digested.[1]

For a typical plant producing 800 tonnes/day of purified terephthalic acid, the flow rate of the aqueous effluent from the crystallization section of the PTA plant coming out of the crystallizer is of the order of $60 \, m^3$/hr. The organic compounds identified in a typical aqueous effluent from crystallization section of the PTA plant kindly supplied by Reliance Industries, India, were benzoic acid, *p*-toluic acid, trimelletic acid, phthalic acid, and *i*-phthalic acid and terephthalic acid. These compounds impose a burden on the effluent treatment plant. Due to the presence of these impurities recycle of aqueous effluent from crystallization section of PTA plant to the terephthalic acid crystallizer is not possible. If the impurities are removed from the aqueous effluent from crystallization section of PTA plant, the load on effluent treatment plant reduces and also aqueous effluent from crystallization section of PTA plant can be recycled resulting in significant saving of process water. This would save water worth $1.5 million per year based on process water cost in India.

There are a number of processes available for the separation and recovery of dissolved organics from aqueous solutions, of which solvent extraction and adsorption are most commonly used. Solvent extraction is preferred when the dissolved solute concentration is relatively high, typically > 1 weight percent. If the dissolved organic concentration is lower (i.e., < 1 weight percent), adsorption is preferred over solvent extraction.[2] Removal of this component by other competing processes may not be economical/possible. All compounds are high boiling/high melting and therefore pervaporation is not suitable. Electrodialysis requires the solutes in an ionic form. To convert the solute acids into salts, an extra base will be needed, increasing the cost and lowering the sustainability of the process. Recently nanofilteration (NF) membranes, which can remove compounds up to 200D (molecular weight), have been commercialized. The compounds under investigation have molecular weight less than 200. Further in a membrane process like RO/NF, the recovery of water is never 100%. As regards solvent extraction (sx) for low concentration of solute, a large quantity of solvents is required. Recovery of solutes from such dilute extract may not be economical. On the other hand

adsorption has the ability to increase solute concentration ranging from several 100 to 1000 fold. Therefore adsorption is attractive at lower concentration.

In recent years, polymeric adsorbents are playing a very important role in recovery and removal of dissolved organics from aqueous solution.[3–6] Adsorption can be carried out using adsorbents (synthetic or natural). Activated carbon and synthetic adsorbents find application in removal of trace organics from aqueous solutions. Both activated carbon and polymeric adsorbents show comparable adsorption capacities. Polymeric adsorbents can be easily regenerated, as the binding affinity between adsorbed solute and polymeric adsorbents is considerably weaker. The main drawback of activated carbon is its inability to desorb completely under mild conditions.[7] Although activated carbon adsorbents were used earlier, their use has diminished due to the complexity and cost of regeneration. A variety of synthetic polymeric adsorbents are available in a wide range of properties (surface area, polarity, porosity, etc.). It has been demonstrated that polymeric adsorbents can separate and recover organic chemicals from aqueous solutions efficiently.[5,8–12]

The aim of this study is to check the feasibility of removal of the organic impurities from the aqueous effluent from crystallization section of PTA plant by adsorption on polymeric resins so that the aqueous effluent from crystallization section of PTA plant can be recycled, resulting in significant saving of process water. The recovery of inorganic compounds (e.g., Cobalt catalyst) can also result in significant saving and subsequently will be studied separately.

EXPERIMENTAL

Materials

For the single solute adsorption studies, synthetic solutions were prepared using a pure sample of the solute. Distilled water was used for preparation of aqueous solutions. The polymeric adsorbents, Amberlite XAD-2, Amberlite XAD-4, and Amberlite XAD-7 were supplied by Rohm and Haas Co. whereas INDION 1014 MN-2 was supplied by Ion Exchange India Ltd. The physical properties of the adsorbents are given in Table 1. Aqueous effluent from the crystallization section of the PTA plant from PTA crystallizer was kindly supplied by Reliance Industries Limited, Patalganga, India. Methanol (Extra Pure) used for washing of the adsorbent was supplied by s.d. Fine Chem. Ltd., India.

Table 1. Characteristics of adsorbents employed.

Adsorbent	Total area (m^2/g)	Pore volume (cm^3/g)	Particle size (mm)	Density (g/cm^3)	Polarity	Polymer matrix
Amberlite XAD-2	300[a]	0.69	0.4	1.02	Nonpolar	Polystyrene–divinylbenzene
Amberlite XAD-4	750[a]	0.99	0.5–0.7	1.03–1.04	Nonpolar	Polystyrene–divinylbenzene
Amberlite XAD-7	450[a]	1.08	0.45–0.6	1.06–1.08	Intermediate	Acrylic ester
INDION 1014 MN-2	1000[b]	1.08	0.3–1.2	1.04	Nonpolar	Polystyrene–divinylbenzene

[a] Rohm and Haas, Inc. Fluid Process Chemicals (2000).
[b] Ion Exchange Ltd. Physical, Chemical and Operating Characteristics: INDION 1014 MN-2. India, (2000).

Adsorbent Preparation

Conditioning of the adsorbent was done by washing it with methanol and then drying at 60°C at 135 Pa absolute pressure. This was done to remove any impurities present in the adsorbent. The vacuum dried adsorbents were stored in sealed flasks to prevent ingress of moisture.

Equilibrium Adsorption Studies

Aqueous solutions of 800 ppm concentration of all the solutes were prepared using distilled water. These were used for single-solute adsorption studies. Fixed amounts of these aqueous solutions ($50*10^{-3}$) were taken in conical flasks and different weights of the adsorbents were added. These flasks were sealed and kept for mechanical shaking at 25°C for 24 hrs till equilibrium was attained. The aqueous solutions were analyzed for their equilibrium concentrations.

The multisolute equilibrium adsorption studies were conducted using the same procedure as that for single-solute adsorption. The aqueous effluent from the crystallization section of the PTA plant mentioned earlier was itself used as the multisolute feed.

Column Exhaustion Studies

The column used for the column exhaustion runs was a glass column, 1500 mm long and 15.6 mm I. D. The column was packed up to 300 mm by preparing a slurry of the adsorbent with water. Methanol followed by distilled water was passed through the column. The aqueous solutions prepared from pure samples were then passed downflow through the column. The flow rate for the breakthrough runs was adjusted to 0.17 bed volumes per minute using a peristaltic pump. Samples were collected periodically and analyzed. For multisolute column exhaustion studies the same procedure was used. In this case aqueous effluent from crystallization section of PTA plant itself was used. The flow rate was adjusted to 0.035 bed volumes per minute for regeneration with acetic acid and methyl acetate being used as the eluants. These eluants are readily available in a PTA plant and hence were the logical choice. Samples were collected and analyzed for the solute content.

Analysis

For single-component studies, the analysis of all the samples was done using Chemito 2100 UV Spectrophotometer. For multisolute adsorption studies, the analysis of all the samples was done using an HPLC system comprising a methanol/aqueous buffer gradient mobile phase, a Novapak C-18 column, and a UV detector at a wavelength of 260 nm. The aqueous buffer was prepared as follows: 50 gms of sodium acetate trihydrate was dissolved in 0.4 L water and then 50% acetic acid was added until a pH of 3.7 was obtained and then the volume was made up to 1 L by deionized water. Out of this solution $50*10^{-3}$ L was taken and again the volume was made up to 1 L by water and used for analysis. The sample to be analyzed was dissolved in excess sodium hydroxide solution and then neutralized by acetic acid. Neutralized sample was injected into the HPLC system. The flow rate of mobile phase was maintained at $1.2*10^{-3}$ L/min. The composition of the mobile phase was adjusted to 12% methanol and 88% aqueous buffer for 0 minutes to 6 minutes, and then between 6 minutes to 12 minutes the composition was changed to 45% methanol and 55% aqueous buffer. This composition of mobile phase was kept constant till the end of analysis of the sample.

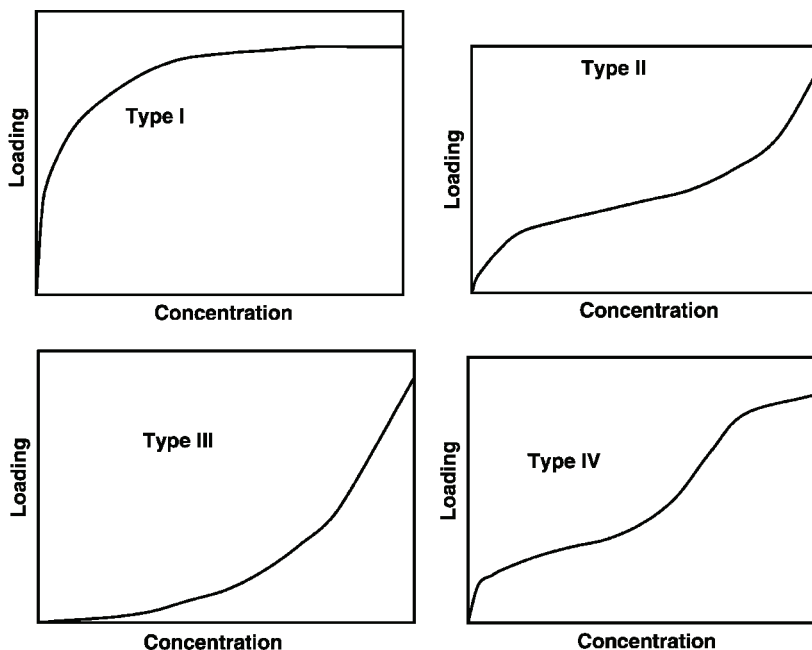Approximately 30% of total experiments were randomly rechecked. The reproducibility was found to be within ±5%.

Figure 1. Types of adsorption isotherms.

The loading capacity, c (mmole/g) was determined from a solute mass balance.[10,11,13] Knowing the initial and final bulk concentrations,

$$c = \frac{(C_o - C_e) \cdot V}{m} \tag{1}$$

The equilibrium adsorption data for single and multisolute adsorption were fitted to the Freundlich isotherms.[14] The Freundlich isotherm:

$$c = m_F C_e^{1/n} \tag{2}$$

The higher the value of m_F and n, the better is the adsorption capacity of the adsorbent. Different types of adsorption isotherms are shown in Fig. 1.[14]

RESULTS AND DISCUSSION

The analysis of the aqueous effluent from crystallization section of the PTA plant was done using HPLC as mentioned earlier. The compounds

detected were *p*-toluic acid (547 ppm), benzoic acid (480 ppm), *i*-phthalic acid (142 ppm), terephthalic acid (336 ppm), phthalic acid (21 ppm), trimelletic acid (196 ppm), cobalt (6 ppm), manganese (16 ppm), iron (0.4 ppm), and chromium (0.1 ppm).

Equilibrium Studies

Single Solute Adsorption Studies

The sorption isotherms were plotted in the conventional manner of loading of adsorbent versus concentration of solute in aqueous phase. Typical isotherms are shown in Fig. 2. The isotherms shown are of Type I, Type II, Type III, and Type IV depending upon the adsorbent and solute.[14] For INDION 1014 IMN-2, isotherms for all the solutes yield Type I isotherm, indicating that adsorption is favorable. The equilibrium adsorption isotherms for single solute adsorption data were fitted to the Freundlich model.[14] The values for the Freundlich constants are given in Table 2. It is clear from Fig. 2 that except for INDION 1014 IMN-2 resin all the other adsorbents can be satisfactorily treated with Freundlich isotherm. INDION 1014 IMN-2 apparently shows a behavior closer to Langmuir isotherm. The best adsorption capacity for all the solutes is obtained with INDION 1014 MN-2. The capacity decreased in the order of decrease in the surface area of the adsorbents: INDION 1014 MN-2 > Amberlite XAD-4 > Amberlite XAD-2 > Amberlite XAD-7. Although the surface area of Amberlite XAD-7 is greater than that of Amberlite XAD-2 the adsorption capacity is less for Amberlite XAD-7 due to its intermediate polarity. The single-solute adsorption isotherms were plotted on the basis of surface concentration (mmole/m^2) versus concentration of solute in the aqueous phase.[4,15] The plots are shown in Fig. 3. For XAD-2 and XAD-4 the amount adsorbed correlates with surface area. However, adsorption of all solutes on INDION 1014 MN-2 was much higher and not in proportion to surface area. As per the manufacturer, a certain proprietary surface treatment is given to the INDION 1014 MN-2, which may be responsible for the higher values of adsorption capacity. Previous work by Amin et al. (2001) on adsorption of alcohols and ketones on INDION 1014 MN-2 and other polymeric adsorbents showed correlation with the surface area. In the present case all the solutes have —COOH group. It is possible that the surface treatment employed for INDION 1014 MN-2 specifically increases the adsorption of hydrophobic acidic solutes.
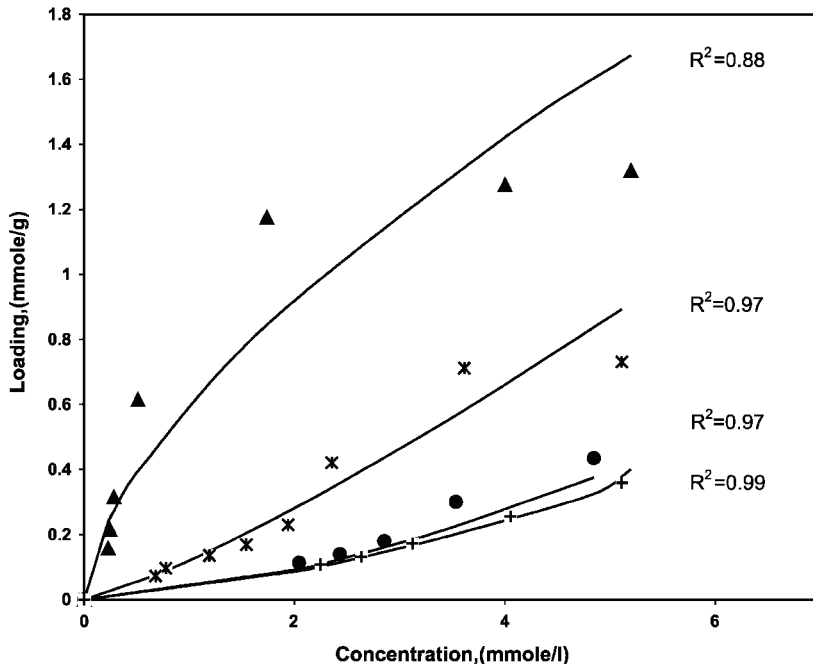
Figure 2. Single-solute adsorption isotherms (loading vs. concentration in liquid) for benzoic acid on various polymeric adsorbents. Temp. $= 25°C$. ●: Amberlite XAD-2; ✻: Amberlite XAD-4; +: Amberlite XAD-7; ▲: INDION 1014 MN-2.

Table 2. Freundlich constants for single solute adsorption studies.

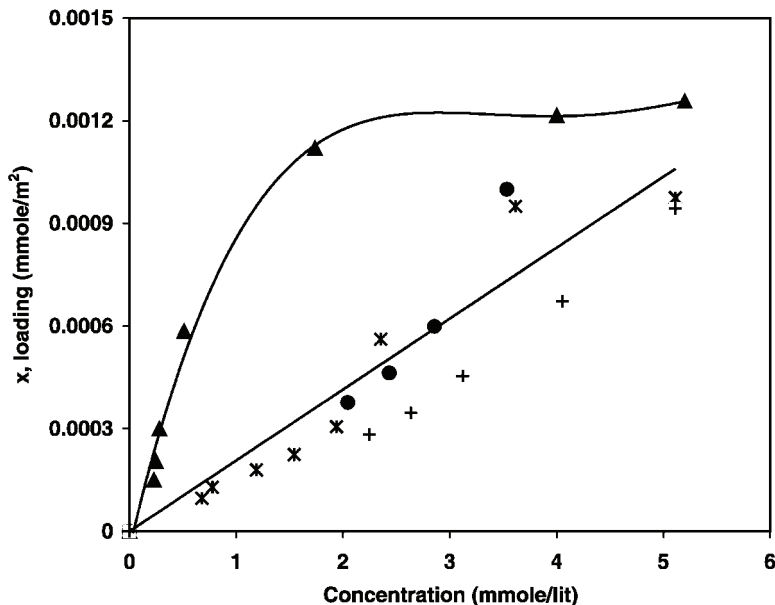|	Adsorbents											
	INDION 1014 IMN-2			Amberlite XAD-4			Amberlite XAD-2			Amberlite XAD-7		
Solute	n	m	R^2	n	m	R^2	n	m	R^2	n	m	R^2
Benzoic acid	1.61	0.6	0.88	0.81	0.12	0.97	0.66	0.03	0.97	0.68	0.03	0.99
p-Toluic acid	1.1	0.77	0.99	0.78	0.16	0.96	0.58	0.14	0.96	0.4	0.138	0.98
Phthalic acid	1.11	0.304	0.88	0.66	0.02	0.97	0.47	0.007	0.99	0.48	0.008	0.97
Trimelletic acid	1.05	0.24	0.89	0.83	0.003	0.93	0.68	0.003	0.96	0.59	0.001	0.97

Figure 3. Single-solute adsorption isotherms (surface concentration vs. concentration in liquid) for benzoic acid on various polymeric adsorbents. Temp. = 25°C. ●: Amberlite XAD-2; ✶: Amberlite XAD-4; +: Amberlite XAD-7; ▲: INDION 1014 MN-2.

Multisolute Adsorption Studies

The sorption isotherms in the case of multisolute adsorption were of Type I, Type II, or Type III, depending upon the adsorbent and solute.[14] Typical isotherms for multisolute adsorption are shown in Fig. 4. An attempt was made to fit the equilibrium adsorption isotherms for the multisolute adsorption data to the Freundlich isotherm.[14] The values of the constants for the Freundlich isotherms are given in Table 3. The overall value of adsorbed concentration of any solute from the mixture was always lower than that for adsorption of a single solute. This is likely to be due to competitive adsorption.[11] Surface occupied by one solute is not available for the other solutes. Thus overall surface availability for any given solute is reduced in the case of adsorption from the mixture.
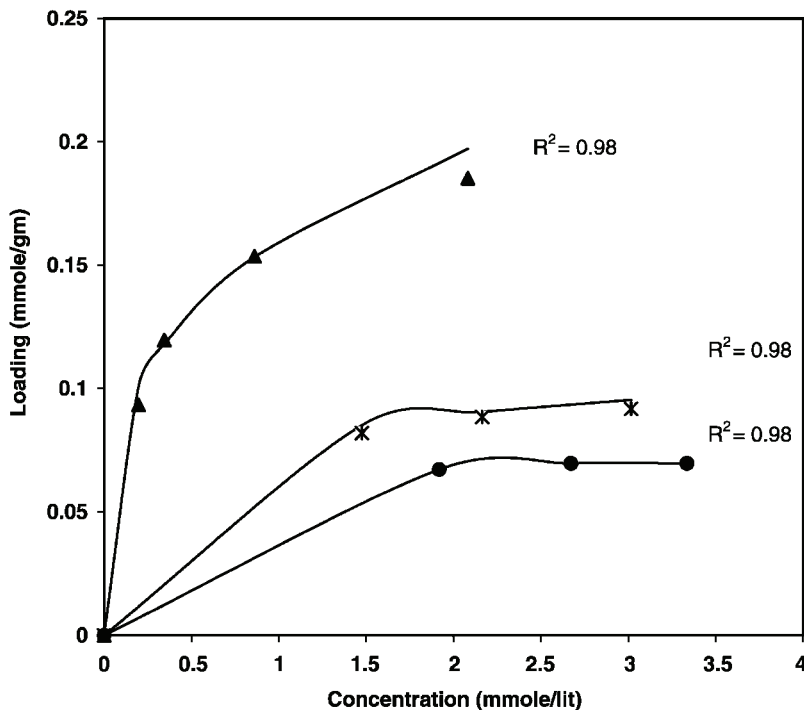
Figure 4. Multisolute adsorption isotherms (loading vs. concentration in liquid) for benzoic acid on various polymeric adsorbents. Temp. = 25°C. ●: Amberlite XAD-2; ✖: Amberlite XAD-4; ▲: INDION 1014 MN-2.

In multisolute adsorption for all the adsorbents it was found that adsorption of trimelletic acid is very low. This may be due to steric hindrance, which may be considered as a sheer physical blockage.[16] The different solutes present are monocarboxylic aromatic acids, dicarboxylic aromatic acids, and tricarboxylic aromatic acid. In the case of tricarboxylic aromatic acid, i.e., trimelletic acid (TMA) the benzene ring is covered by three —COOH groups at 2, 4, 6 positions. TMA is much bulkier as compared to other solutes, which may be responsible for poor adsorption because the adsorption surface may favor less bulkier solutes. This may be the reason for poor adsorption of trimelletic acid in the presence of other solutes as the competition for adsorption sites is significant.

Table 3. Freundlich constants for multisolute adsorption studies.

Solute		IMN-2			XAD-4			XAD-7	
	n	m	R^2	n	m	R^2	n	m	R^2
Benzoic acid	3.5	0.16	0.98	6.26	0.08	0.97	4.76	0.07	0.99
p-Toluic acid	2.77	0.36	0.98	1.96	0.16	0.99	1.07	0.96	0.96
Phthalic acid	0.78	0.51	0.99	0.41	0.88	0.97	0.47	0.18	0.98
Isophthalic acid	3.33	0.15	0.81	1.6	0.004	0.36	2.1	0.04	0.72
Terephthalic acid	6.66	0.02	0.9	1.96	0.08	0.72	0.59	0.003	0.99

Column Exhaustion Studies

From the single solute and multisolute equilibrium studies it is clear that INDION 1014 MN-2 shows best adsorption capacity; hence column exhaustion and regeneration studies were carried out only for INDION 1014 MN-2.

Breakthrough

The plots for single-solute and multisolute studies are shown in Figs. 5 and 6. The capacities at breakpoint and saturation point are given in Tables 4 and 5. In multisolute column adsorption trimelletic acid is not adsorbed but shows adsorption when present alone, as is evident from single-solute adsorption studies. To remove all the solutes from the aqueous effluent from the crystallization section of the PTA plant, two columns operating in series can be used. It is imperative to operate the first column up to breakpoint with respect to solutes other than trimelletic acid only. All solutes except TMA will get adsorbed in the first column, whereas TMA does not show significant adsorption in the presence of other solutes. The second column containing fresh adsorbent can be fed by the effluent from the first column, which is devoid of all solutes except TMA. Thus, the second column will operate as if it is receiving only TMA and remove it.
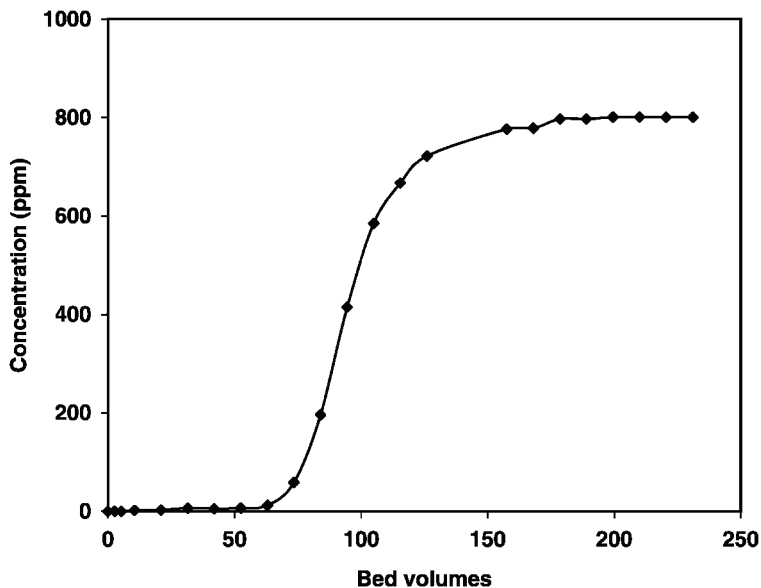
Figure 5. Single-solute breakthrough curve for benzoic acid adsorption on INDION 1014 MN-2. Temp. = 25°C. Feed concentration = 800 ppm. Mass of adsorbent = 60 g.

Regeneration

   Acetic acid and methyl acetate are readily available in a PTA plant. Acetic acid is used as a solvent in the oxidation of *p*-xylene and methyl acetate is produced as a byproduct in the plant. Hence the regeneration studies for single-solute and multisolutes were carried out using acetic acid and methyl acetate. The plots for single-solute and multisolute studies are shown in Figs. 7 and 8, respectively. The initial load, rest load (i.e., amount of solute present on adsorbent after regeneration), and mass of adsorbent used are given in the Tables 6 and 7. In both the cases complete regeneration of the exhausted bed was possible using 3 to 5 bed volumes of solvents. The concentrations of the compounds in the regeneration samples were much higher compared with concentrations in the original aqueous effluent from a crystallization section of the PTA plant. Thus for benzoic acid the original concentration in the aqueous effluent from a crystallization section of the PTA plant was 0.48 gm/lit whereas the concentration of benzoic acid in total eluant at complete
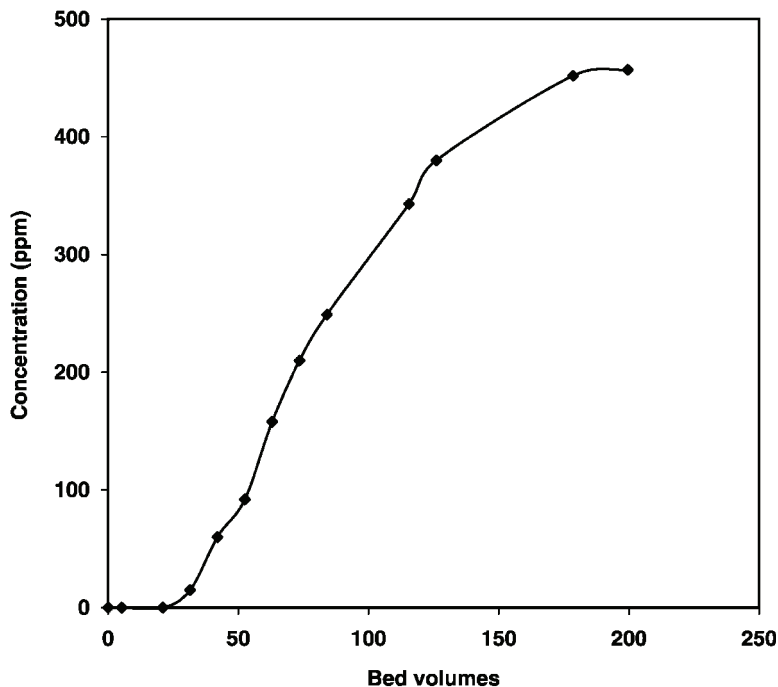
Figure 6. Multisolute breakthrough curve for benzoic acid adsorption on INDION 1014 MN-2. Temp. = 25°C. Feed concentration = 480 ppm. Mass of adsorbent = 60 g.

Table 4. Capacity at breakpoint and saturation point for single solute adsorption (INDION 1014 MN-2 Resin).

Solute	Capacity at breakpoint (moles/gm of resin) $\times 10^4$	Capacity at saturation point (moles/gm of resin) $\times 10^4$
p-Toluic acid	4.04	6.85
Benzoic acid	4.34	6.07
Trimelletic acid	0.38	1.24
Phthalic acid	1.33	3.02

Table 5. Capacity at breakpoint and saturation point for multisolute adsorption (INDION 1014 MN-2 Resin).

Solute	Capacity at breakpoint (moles/gm of resin) $\times 10^4$	Capacity at saturation point (moles/gm of resin) $\times 10^4$
p-Toluic acid	1.63	4.04
Benzoic acid	1.23	3.03
Phthalic acid	0.008	0.01
i-Phthalic acid	0.084	0.24
t-Phthalic acid	0.012	0.12
Trimelletic acid	0	0

Figure 7. Single-solute regeneration curve for benzoic acid with acetic acid and methyl acetate on INDION 1014 MN-2. Temp. = 25°C. ■: Acetic acid; ✳: Methyl acetate.

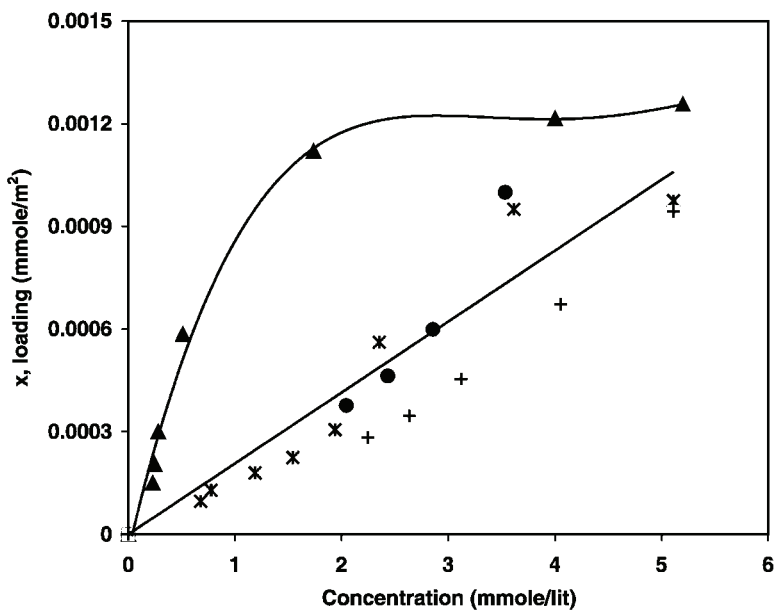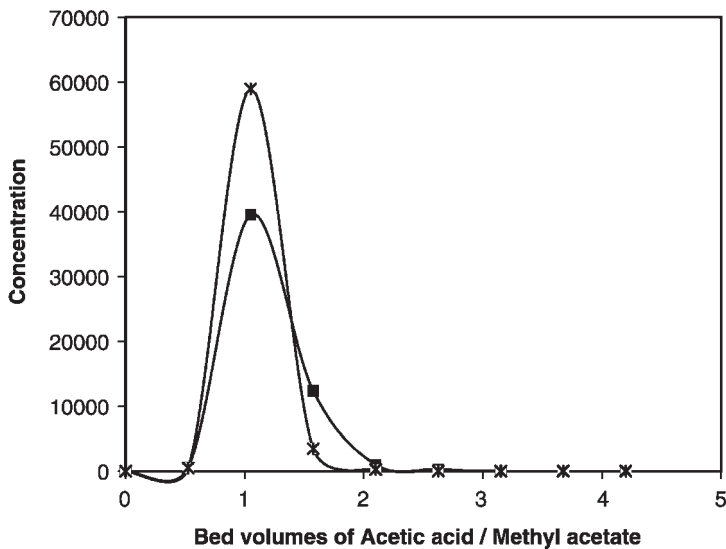*Figure 8.* Multisolute regeneration curve for benzoic acid with acetic acid and methyl acetate on INDION 1014 MN-2. Temp. = 25°C. ■: Acetic acid; ✳: Methyl acetate.

Table 6. Values of initial load, rest load, and mass of adsorbent used for single solute desorption (INDION 1014 MN-2 Resin).

Solute	Initial load, gm	Bed volumes of regenerant for complete regeneration		Rest load, gm	Mass of adsorbent used, gm
		Acetic acid	Methyl acetate		
p-Toluic acid	5.076	3	2	0	60
Benzoic acid	4.44	3	2.8	0	60
Phthalic acid	3.003	2.8	2.2	0	60
Trimelletic acid	1.536	3	2	0	60

Table 7. Values of initial load, rest load, and mass of adsorbent used for multisolute desorption.

| Solute | Initial load, gm | Bed volumes of regenerant for complete regeneration | | Rest load, gm | Mass of adsorbent used, gm |
		Acetic acid	Methyl acetate		
p-Toluic acid	3.20	3.2	2.7	0	60
Benzoic acid	2.25	2.3	2.2	0	60
Phthalic acid	0.02	1.8	1.6	0	60
i-Phthalic acid	0.23	3.2	2.5	0	60
t-Phthalic acid	0.09	2.5	2.5	0	60
Trimelletic acid	0	0	0	0	60

regeneration was in acetic acid: 17.19 gm/lit and in methyl acetate 18.34 gm/lit.

This indicates that the adsorbents are separating organics from water and concentrating them simultaneously. Methyl acetate was found to be a better solvent for regeneration because for methyl acetate comparatively less amount was required for complete regeneration and hence higher concentrations of the solutes were obtained. Further, methyl acetate is much lower boiling and noncorrosive. The lower boiling point allows better solvent stripping.

CONCLUSION

A systematic study of adsorptive recovery of various organic compounds found in PTA plant effluent was carried out. The polymeric adsorbents used were INDION 1014 MN-2, Amberlite XAD-2, Amberlite XAD-4, Amberlite XAD-7. Single and multisolute equilibrium and column breakthrough studies showed that amongst the various adsorbents INDION 1014 MN-2 yielded the highest capacity. When present alone trimelletic acid showed adsorption while its sorption was poor in the presence of other solutes. In view of this a two-column system configuration has been suggested. Amongst the regenerants tried, methyl acetate was found to be better than acetic acid. The results indicate that it is feasible to remove organic compounds from PTA plant effluent. However this effluent also contains other inorganic compounds like compounds of cobalt, manganese, etc. A complete recycle of aqueous effluent

from a crystallization section of the PTA plant as process water would require a separate study concerning these compounds.

NOMENCLATURE

C_e	equilibrium concentration of solute (mmole/L) or (ppm)
C_o	initial concentration of solute (mmole/L) or (ppm)
m	mass of the adsorbent (g)
m_F	Freundlich constant
n	Freundlich constant
V	volume of solution taken liter (L)
c	loading on the adsorbent (mmole/g)
x	surface loading of the solute on the adsorbent mmole/m^2

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