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Removal of Surfactants from Effluents

Removal of Non-Ionic and Anionic Surfactants from Effluents Intended for Reuse

Physikalisch-chemische Behandlungsverfahren wurden hinsichtlich ihrer Wirksamkeit bei der Eliminierung von nichtionischen und anionischen Tensiden aus Kläranlagenabläufen geprüft. Flockulierung mit Eisen(III)-chlorid ergab eine Eliminierung von 79%; eine Batchadsorption mit Hilfe dreier verschiedener Aktivkohlen brachte 90% Eliminierung bei den anionischen und mehr als 95% Eliminierung bei den nichtionischen Tensiden. Als effektivster Weg bei der praktischen Anwendung erwies sich die kontinuierliche Flockulierung mit anschließender Sandfiltration und darauffolgender Adsorption.

Physical-chemical treatments were assessed for their impact on the removal of non-ionic and anionic surfactants from sewage treatment plant effluents. Flocculation with ferric chloride achieved 79% removal whilst a batch adsorption of three types of activated carbon achieved 90% removal of anionic, and over 95% removal of non-ionic surfactants. For a practical on-site removal of these compounds from effluent, a continuous flow of flocculated effluent, followed by sand filtration and adsorption through a bed of selected granular activated carbon, proves a most effective means for the removal of non-biodegradable non-ionic and anionic surfactants.

1 Introduction

The abundance of non-ionic surfactants, NIS, incorporated into domestic and industrial cleaning agents, continues to expand and encourages studies of their fate in municipal wastewater [1, 2] especially where such water is to be re-used for irrigation and fish ponds. Independent studies have demonstrated the toxicity of these compounds to fish [3] and crops [4], whilst the so-called biodegradable forms of NIS are known to produce toxic residues [5]. For example, chlorinated nonyl phenol ethoxylates have been detected in the American River Delaware by *Sheldon* and *Hites* [6] along with alkyl phenols, the incompletely biodegraded forms of alkyl phenol ethoxylated non-ionic surfactants.

In our local, Haifa Municipal Sewage Treatment Plant, relatively high concentrations of non-ionic and anionic surfactants are found in the raw sewage and biologically treated effluents. The once familiar foaming problems generated by large residual surfactants in effluents, treatment plants and rivers have all but subsided. However, the current concentrations in the biologically treated effluents at the sewage treatment plant indicate the continued use of ABS and of non-biodegradable NIS. The source of the latter would appear to be the enhancement of detergent properties by certain local industries who add dinonyl phenol polyethoxylate, DNP, to their formulations. The general seriousness of these problems has even been recognised by the Standard Methods for the Analysis of Water and Wastewater, who have included the measurement of non-ionic surfactants in their latest edition [7].

In Israel, where great emphasis is placed on the reclamation of sewage treatment plant effluents for irrigation, fish ponds and industry, the expansion of this technology in the future will depend very much on the ability to remove toxic residues, such as hard non-ionic surfactants from these effluents. With this in mind, the current research set out to investigate the removal of non-biodegradable surfactants from biologically treated effluents by physical-chemical methods.

2 Experimental

2.1 Materials

Two non-biodegradable surfactants were selected for this study:

Berol 716 - a non-ionic surfactant, dinonyl phenol polyethoxylate, DNP, whose predominant oligomer contains an ethoxylate chain length of 16 ethylene oxide units. It has an average molecular weight of 1029. This material was procured from Vitco Ltd, Haifa, and is the product of Berol Kemi AB, Sweden. The probable cause of its resistance to biological degradation is the presence of the two branched-chain nonyl functions substituted onto the aromatic ring of the phenol.

Alkyl Benzene Sulphonate (ABS) - an anionic surfactant whose principal component is a branched chain alkyl benzene sulphonate of molecular weight 348 and is the product of the Soap and Detergent Association, New York, U.S.A.

The biological effluents used in this study were obtained by grab sampling from the secondary settling ponds following trickling filters and activated sludge treatments at the Haifa Municipal Sewage Treatment Plant.

For the purpose of comparison and interpretation, experiments conducted in aqueous solutions employed a simulated local tap water. These controlled synthetic solutions were prepared with the following salt concentrations in distilled water:

Na_2SO_4 – 1 meq/L,
$NaHCO_3$ – 6 meq/L,
$CaCl_2$ – 4 meq/L,
$MgCl_2$ – 4 meq/L

The three flocculants assessed included cationic and anionic polyelectrolytes, products of Dow Chemicals, U.S.A., as well as alum, lime and ferric chloride, products of B.D.H Chemicals Ltd., Poole, England. Adsorption was carried out on two granular activated carbons, Filtrasorb (F 300) and Filtrasorb 400 (F 400) both products of the Calgon Corporation, Michigan, U.S.A. Also used was a powdered activated carbon (PAC) the product of B.D.H. Chemicals Ltd.

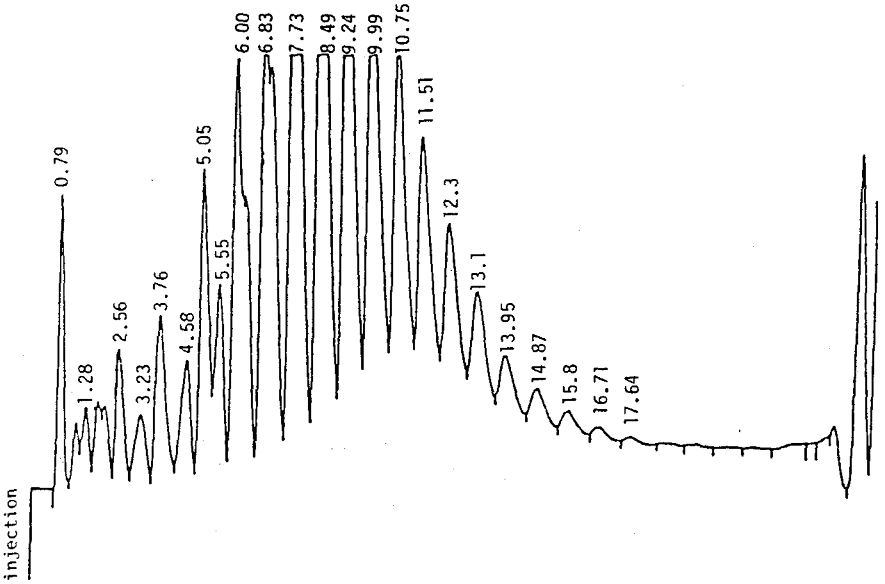

Fig. 1. HPLC of dinonyl phenol ethoxylate extracted from aqueous solution

2.2 Methods

The effluents from the activated sludge and trickling filter settling ponds were analysed for surfactant residues on each sampling occasion. ABS was measured according to the Standard Method for its analysis [7] and NIS was analysed according to the *Wickbold* method [8]. The soluble fraction of effluents was obtained after filtration through Whatman 4V filter paper. The physical-chemical treatments assessed were flocculation, sedimentation and filtration followed by batch adsorption on activated carbon. The results of these experiments were then used to select the most effective continuous flow system utilising a combination of these treatments. The activated carbon column used in this system employed the following parameters:

Column diameter = 2 cm Bed depth = 67 cm
Wet carbon volume = 250 cm^3 Carbon weight = 140 g
Flow rate = 5 bed volumes per hour

In order to sucessfully gauge the effective removal of DNP from effluents, the effluent was initially dosed with 10 mg/L DNP to enable a competent analysis of the residual surfactant following treatment. Similar experiments were undertaken on controlled synthetic aqueous solutions dosed with 10 mg/L DNP to enable interpretation of the former results.

3 Results and Discussion

3.1 HPLC Analysis

Justification for the selection of DNP as a model NIS for this study comes from an HPLC analysis of an ethyl acetate extract of trickling filters' effluent from the Haifa Municipal Sewage Treatment Plant (figures 1 and 2). The extract was obtained by sublimation according to the *Wickbold* technique [8]. This chromatogram was compared with that obtained from the extraction of 10 mg/L DNP in aqueous solution and shows that among the non-ionic surfactants found in the effluent, DNP is the main constituent due to its non biodegradability. Both extracts were chromatographed in the laboratories of Dr. *W. Giger* of EAWAG, Dubendorf, Switzerland by normal-phase HPLC [9].

3.2 Sewage Treatment Survey

The Haifa Municipal Sewage Treatment plant has been monitored for both anionic and non-ionic surfactant concentrations for more than 10 years. Prior to 1975, 20-25 mg/L ABS were regularly found in the total effluents content [2] while today, 8-11 mg/L are found in raw sewage with 4-6 mg/L in the biologically treated effluent. The concentration of NIS in raw sewage has declined to a much lesser extent in the last decade, from up to 10 mg/L in 1976 [10] to 4-8 mg/L in the present study. With regards to the trickling filters' effluents, the NIS concentration have dropped from 4 mg/L in 1976 to about 1 mg/L in this survey. A typical analysis is presented in Table 1.

The results of these analyses are an indication of the fate of surfactants in the sewage treatment plant. The first indication is that due to the introduction of new biodegradable Zoharex NIS and linear alkyl benzene sulphonate (LAS) in major locally formulated washing powders, the residual NIS and ABS concentrations in effluents has fallen dramatically in the last 10 years. The NIS actually remaining in the secondary effluents and identified mostly as DNP, results from the addition of this compound to these newly formulated detergents by the relevant industries.

A second indication is that the activated sludge plant is the most effective biological treatment for the removal of both types of surfactants. However, during the period of these experiments, the activated sludge plant only operated intermittently and encountered numerous technical problems. Hence, trickling filters' effluent was employed in our laboratories. A major conclusion from these analyses is that the larger proportion of surfactants are adsorbed onto the suspended solids content of raw sewage. This is indicated by the substantial reduction of surfactants' concen-

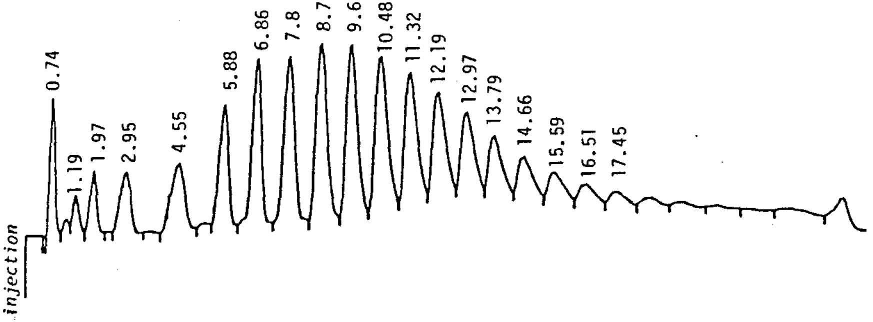

Fig. 2. HPLC of extract from trickling filter effluent

Table 1. Sewage Treatment Plant Analysis

Parameter	Units	R.S. Tot.	R.S. Diss.	T.F. Tot.	T.F. Diss.	A.S. Tot.	A.S. Diss.
COD	mg/L as O_2	842	295	206	177	105	73
BOD_5	mg/L as O_2	325	124.8	56.6	28.2	7.5	3.5
Anionic MBAS	mg/L as ABS	7.5	4.1	4.0	3.5	2.1	0.8
NIS	mg/L as DNP	4.4	2.5	1.9	0.7	0.8	0.4

* R.S. = Raw Sewage; T.F. = Trickling Filters' Effluent; A.S. = Activated Sludge Effluent; Tot. = Total Fraction; Diss. = Dissolved Fraction

tration in the soluble fraction as compared to the total fraction; more than 40% of the total ABS and total NIS remains in the soluble fraction of raw sewage with up to 50% adsorption on the suspended solids content of effluents.

3.3 Flocculation

In the light of this result, flocculation was selected as the physical-chemical treatment applied to trickling filters' effluents to enhance suspended solids removal with the consequent removal of NIS adsorbed upon them and to assist in the removal of the soluble NIS fraction.

A selection of flocculants were assessed for their effectiveness on the removal of DNP from aqueous synthetic solutions dosed with 10 mg/L DNP. The most effective flocculant was then applied to trickling filters' effluents to which DNP was added to raise its initial concentration to 10 mg/L. The combined results are presented in table 2.

In both cases, ferric chloride appears to be the most effective flocculant, removing 58% DNP from aqueous solutions but rising to 79% in effluent, at a slightly reduced optimum dose. As was shown in table 1, part of the non-ionic surfactants are adsorbed on the suspended solids and during flocculation, when suspended solids are removed, previously adsorbed non-ionic surfactants are removed with the suspended solids together with NIS in solution. The experiments in aqueous solution have already shown that ferric chloride can remove the NIS in this way.

Ferric chloride hydrolyses in water into ferric polyhydroxocomplexes which act as flocculant. The mechanism of flocculation with these complexes is usually partial charge neutralisation and bridging. This can account for the flocculation of suspended solids in effluents which results in the removal of NIS already adsorbed on them. In addition, there is interaction between flocculant and soluble NIS in both aqueous and effluent media. In this case, charge neutralisation cannot be responsible for the mechanism since non-ionic surfactants are neutral. Instead, adsorption and bridging occurs between precipitating ferric polyhyroxocomplexes and the non-ionic surfactant. The interactions are by hydrogen bonding of the etheral groups of the hydrophilic polyethoxylate in the NIS molecule with the hydroxyl groups on the ferric polyhydroxocomplexes. The removal of soluble NIS in this way is the sweep coagulation mechanism. Additionally, the polyhydroxocomplexes, which have already flocculated the suspended solids, can themselves interact with soluble NIS to provide a further mechanism for their removal by adsorption and bridging. Consequently, the efficiency of DNP removal from effluents is higher than in aqueous solution.

These results allowed us to select the optimal dose of ferric chloride, namely 200 mg/L, as a pretreatment for all further physical treatments assessed, namely sand filtration and activated carbon adsorption.

3.4 Batch Carbon Adsorption

As flocculation was unable to completely remove the non-ionic surfactants from effluents, adsorption on two granular activated carbons Filtrasorb 300 (F 300) and Filtrasorb 400 (F 400), and one powdered activated carbon (PAC) was undertaken on the flocculated, sand-filtered effluents. An additional quantity of DNP was added to the flocculated effluents to raise the initial DNP concentration to 10 mg/L. Similar experiments were then carried out on synthetic aqueous solutions to verify and interpret the results. The maximum adsorptive capacities Q_0 were determined through batch adsorption isotherms. Q_e, the amount of surfactant adsorbed per unit weight of adsorbent in equlilbrium with a solution of concentration C, was plotted against C, which in this case is the residual surfactant concentration. The general isotherms thus obtained for effluents are shown in figures 3 and 4.

The S-shaped isotherm obtained in the adsorption of DNP from effluent onto PAC (fig 4) was first linearized according to the BET model associated with multi-layer adsorption [11]. However, a break appeared in the curve (fig 5) which aroused suspicions over the behaviour of DNP ad-

Table 2. The Effect of Flocculants on the Removal of Dinonyl Phenol Polyethoxylate (10 mg/L) from Aqueous Solutions and Effluents

Flocculant	Type	Medium	Final pH	Optimum Dose mg/L	Removal Efficiency %
Purifloc C-31	Cationic	Aqueous	8.0	2.0	16.8
Purifloc C-32	Cationic	Aqueous	7.9	up to 10.0	0
Purifloc A-23	Cationic	Aqueous	8.0	2.5	30.5
Separan AP-30	Anionic	Aqueous	8.0	2.5	27.0
Purifloc XD 8494	Cationic	Aqueous Effluent	8.0 7.9	8.0 19.0	41.0 40.7
Lime		Aqueous Effluent	11.4 10.8	720 800	11.2 53.9
Alum		Aqueous Effluent	6.2 5.9	250 200	9.3 40.0
Ferric Chloride		Aqueous Effluent	5.2 5.9	230 200	58.0 79.0

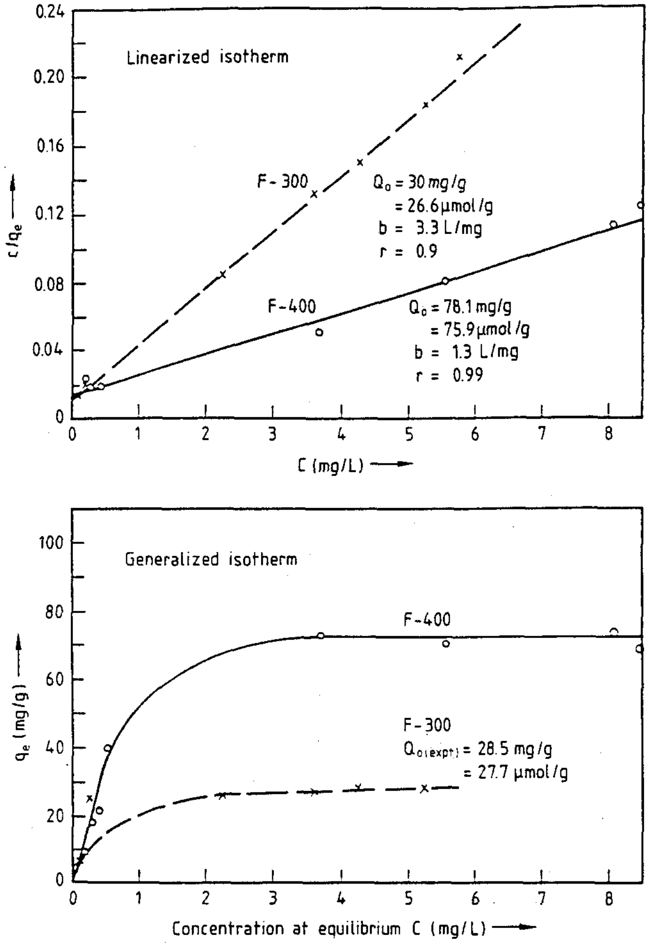

Fig. 3. Langmuir isotherms of DNP adsorption from effluent by F300 and F400

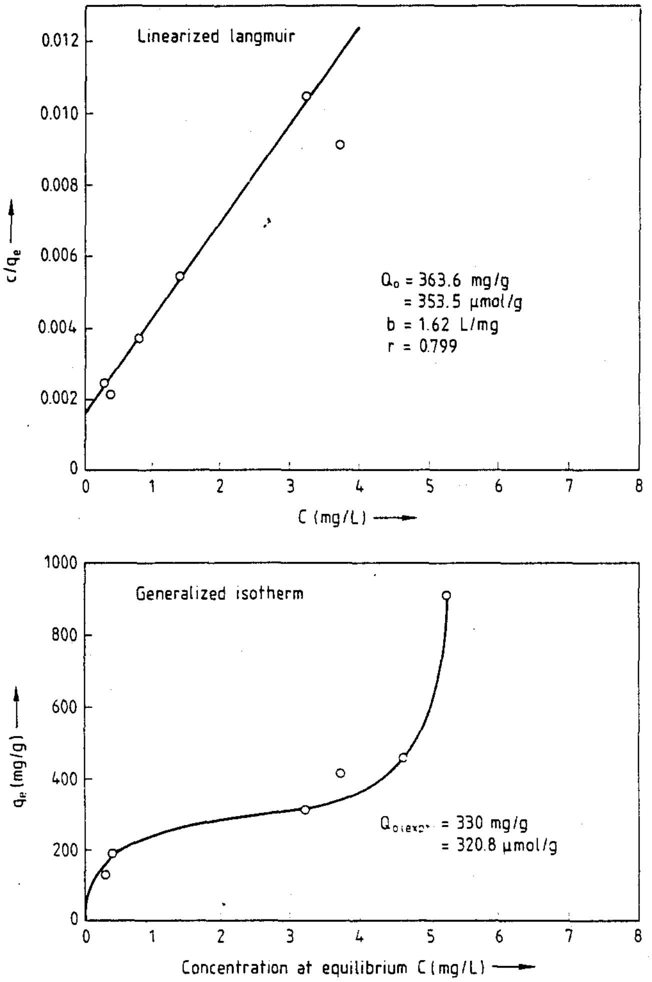

Fig. 4. General and Langmuir isotherm of DNP adsorption from effluent on PAC

sorption according to simple layer upon layer as in the BET model.

Similar cases have occurred with the adsorption of other non-ionic surfactants from aqueous solutions [12]. The breaks in this instance also showed that the BET model did not sufficiently explain the S-type isotherms obtained from NIS adsorption on activated carbons. The Langmuir treatment is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The BET model assumes that a number of layers of adsorbate are formed at the surface and that the Langmuir equation applies to each layer. It was therefore assumed that the first monomolecular layer in the BET model can be treated according to a Langmuir model up to the inflection point on the S-type curve. Beyond this point it was assumed that additional layers of solute molecules begin to accumulate on the previously adsorbed molecules.

Consequently, linearization of the results up to the point of inflection on the generalised isotherm by the Langmuir model allowed for the evaluation of the maximum adsorptive capacities, Q_0, for the formation of a monolayer on the carbon surface. A comparison of the values of Q_0 obtained from both BET and Langmuir linearizations show a higher value in the case of the Langmuir model.

Neither of these adsorption mechanisms can adequately describe the adsorption process and it seems that micelle formation contributes to the process. The hydrophobic character of the surfactant molecule strengthens its adsorption affinity to activated carbon. This in turn can result in an accumulation of individual DNP molecules onto the adsorbent surface building a monolayer with subsequent attachment of surfactant molecules which contribute to localised micelle formation on the carbon surface. Alternatively, micelles could be produced within the solution and adsorbed as such. In these cases, adsorption of micelles would occur rather than of individual DNP molecules. Such mechanisms have been previously postulated by *Carberry* et al. [13] for the

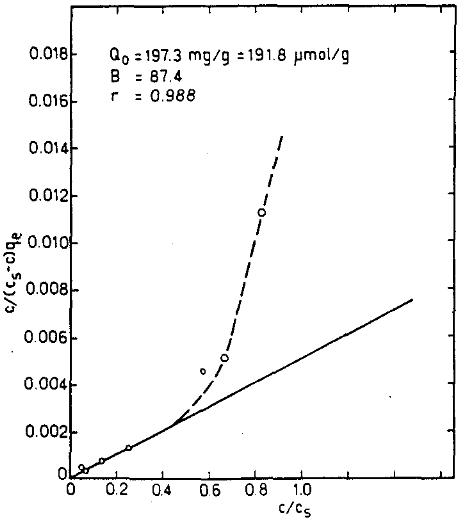

Fig. 5. BET isotherm of DNP adsorption from effluent on PAC

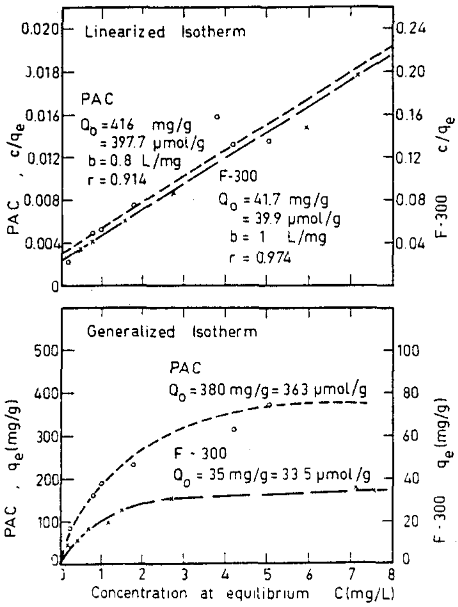

Fig. 6. Langmuir isotherms of DNP adsorption from aqueous solution by F300 and PAC

adsorption of tetrahydrofuran polyethoxylated non-ionic surfactants. It is not clear which of these mechanisms is responsible for DNP adsorption on activated carbon.

In comparing aqueous adsorption to that from effluent, the variety of soluble organics present in the latter medium will compete for adsorbent sites, thus reducing the value of Q_0 for DNP in effluent. This is observed in the case of DNP adsorption on granular F 300 in aqueous solution (fig 6) where Q_0 is 39.9 µmol/g. This is reduced to 28.7 µmol/g for effluent adsorption on the same carbon.

A similar effect is noted for DNP adsorption on F 400 with the values of Q_0 137 µmol/g for aqueous medium reduced to 75.9 µmol/g in effluent (figs 3 and 7).

PAC with its 10-fold larger surface area [14] offers the largest values of Q_0, 363 µmol/g in aqueous solution (fig 4) reduced to 191.8 µmol/g by BET linearization (fig 5).

With regards anionic surfactant (ABS) in effluent, an initial concentration of 10 mg/L produced a Langmuir adsorption isotherm with a value for Q_0 of 21.55 µmol/g on F 400 (fig 8).

The asymptotic generalised Langmuir isotherm obtained for ABS indicates a monolayer adsorption mechanism with larger adsorbent doses required for its removal from effluent than DNP. This also indicates that a continuous flow process for adsorption of these compounds from effluents is unlikely to be as efficient for ABS as for DNP.

3.5 *Continuous Flow Adsorption*

As Filtrasorb (F 400) showed the highest maximum adsorptive capacity of the two granular activated carbons assessed towards DNP, it was selected in a continuous flow adsorption of DNP from flocculated, sand-filtered effluent. An estimation of column exhaustion for surfactant on F 400 may be calculated using the adsorption constants obtained from the appropriate batch adsorption isotherms. This helps in assessing the potential monitoring period of the continuous flow process.

$$Q_0 = \frac{(C_0 - C)\,V}{w}$$

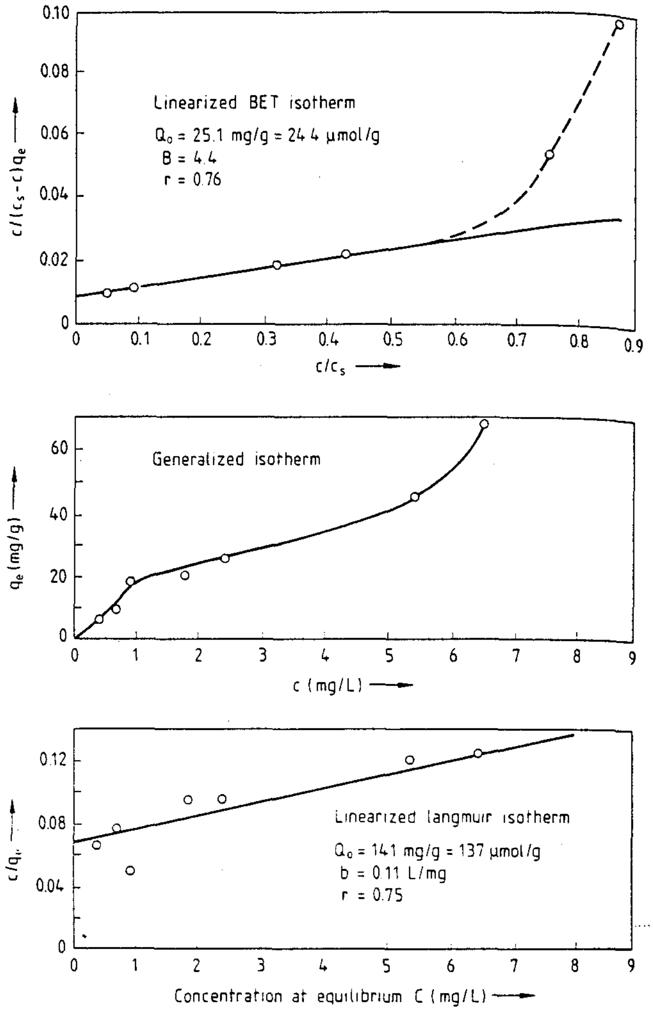

Fig. 7. Adsorption isotherms for DNP in aqueous solution on F400

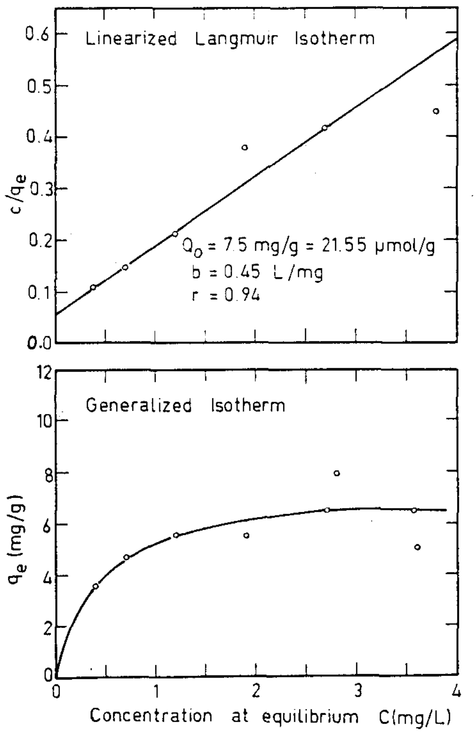

Fig. 8. Langmuir isotherm for ABS in effluent on F400

where

Q_0 = maximum adsorptive capacity for surfactant on F 400 (78.1 mg/g for DNP, 7.5 mg/g for ABS)
C_0 = input surfactant concentration (5 mg/L for DNP, 2 mg/L for ABS)
C = required output concentration (0 mg/L)
w = weight of carbon in column (140 g)
V = total throughput volume (litres)

For a bed volume of 250 cm^3 this results in a calculated throughput of 8750 bed volumes of effluent for breakthrough of DNP and 2100 bed volumes in the case of ABS. The continuous adsorption breakthrough curves are shown in figure 7 in which immediate leakage of organics occur, as determined by residual COD for which C/C_0 is immediately 0.47.

Breakthrough of ABS occurs at 2000 bed volumes which is reflected in a second breakthrough of COD and shows good correlation with the calculated breakthrough. The actual increase in COD exceeds that due to ABS alone according to theoretical COD calculations. Thus ABS is assisting in the removal of organics from solution by a bridging mechanism between the soluble organics and the activated carbon. Breakthrough for DNP occurs after 10000 bed volumes and a similar effect on COD is observed. The calculated breakthrough, being less than this value indicates a lower than realistic evaluation of Q_0 for DNP adsorption on F 400 from effluent in the batch adsorption experiments. This adds credance to our postulation of micelle adsorption which would increase the effective value of Q_0 above that evaluated here for a linearized Langmuir isotherm.

At a throughput of 5 bed volumes per hour on a laboratory scale, an 80 day continuous flow operation involving adsorption of flocculated effluents containing a residual 10 mg/L dinonyl phenol ethoxylate was possible before breakthrough of DNP occured. On this basis, the operation would translate effectively into an on-site removal process for both ABS and DNP removal from flocculated sand-filtered secondary effluents by use of granular activated Filtrasorb 400 carbon. This combined system is therefore to be recommended for the complete removal of non-biodegradable surfactants in the form of ABS and DNP from effluents destined for reuse.

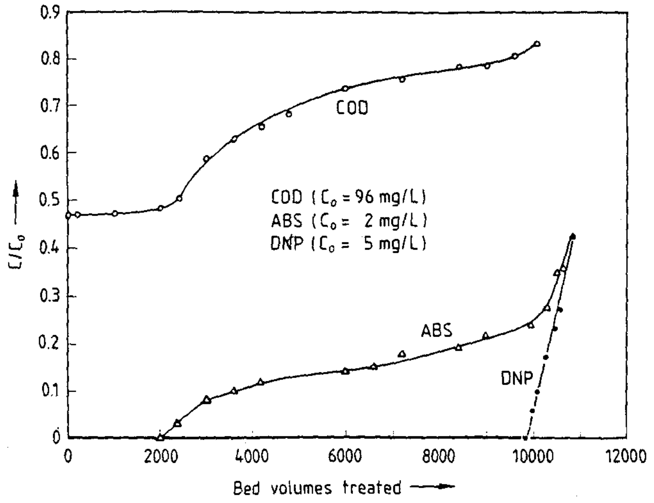

Fig. 9. Breakthrough curves for ABS, DNP and COD from effluent on F400

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