Int. J. Chem. Technol. **2022**, 6 (1), 1- 6

DOI: http://dx.doi.org/10.32571/ijct.986667 E-ISSN: 2602-277X

International Journal of Chemistry and Technology

http://dergipark.org.tr/ijct

Research Article

Optimization of extraction parameters of cationic dye using emulsified liquid membrane process. Application of Box-Behnken design

Salima BENDEBANE[1,2,*], Hawa BENDEBANE[1,4], Farida BENDEBANE[1,3], Fadhel ISMAIL[1,5]

[1]Laboratory LOMOP,

[2]National Higher School of Mines and Metallurgy, Ammar laskri-Annaba

[3]Department of Chemistry

[4]Laboratory LNCTS, [5]Department of Process Engineering, University Badji-Mokhtar of Annaba

Received: 24 August April 2021; Revised: 1 February 2022; Accepted: 4 February 2022

***Corresponding author e-mail: salima.bendebane@ensmm-annaba.dz

Citation: Bendebane, S.; Bendebane, H.; Bendebane, F.; Ismail, F. *Int. J. Chem. Technol.* **2022**, 6 (1), 1-6.

ABSTRACT

Cationic dye (Methylene blue) was extracted from wastewater by using emulsified liquid membrane process. The membrane is composed of two phases: organic and aqueous. D2EHPA, SPAN 80, and acid are the composition of the aqueous phase, however, the fuel oil represents the organic phase. The effect of different parameters such as the initial concentration of cationic dye (MB), the addition of salt (KCl/ NaCl/ Na_2SO_4), acid (HCl/ H_2SO_4/H_3PO_4) and the extractant concentration (10, 30 and 50 ppm) was examined using Box-Behnken design. The optimization of the extraction has been shown that the extraction efficiency reach100% for the following optimum operating conditions: 30 ppm for the initial concentration of $[BM]_0$, 10%w for the extracting (D2EHPA) with the presence of Na_2SO_4 and H_2SO_4. It can be said that the ELM method is efficient for the removal of methylene bleu.

Keywords: Emulsified liquid membrane, extraction, methylene bleu, modelling, optimization.

Emülsifiye sıvı membran prosesi kullanılarak katyonik boyanın ekstraksiyon parametrelerinin optimizasyonu. Box-Behnken tasarımının uygulanması

ÖZ

Emülsifiye sıvı membran prosesi kullanılarak atık sudan Katyonik boya (Metilen mavisi) ekstrakte edilmiştir. Membran organik ve sulu olmak üzere iki fazdan oluşmaktadır. Sulu fazın bileşiminde D2EHPA, SPAN 80 ve asit bulunur, ancak fuel oil organik fazı temsil eder. Katyonik boyanın başlangıç konsantrasyonu (MB), tuz ilavesi (KCl/ NaCl/ Na2SO4), asit (HCl/ H2SO4/H3PO4) ve ekstraktan konsantrasyonu (10, 30 ve 50 ppm) gibi farklı parametrelerin etkisi Box-Behnken tasarımı kullanılarak incelenmiştir. Ekstraksiyonun optimizasyonu aşağıdaki optimum çalışma koşulları için ekstraksiyon verimliliğinin %100'e ulaştığını göstermiştir: 30 ppm [BM]0 başlangıç konsantrasyonu, Na_2SO_4 ve H_2SO_4 varlığında yapılan ekstraksiyonun %10'u (D2EHPA). Metilen mavisinin giderilmesinde ELM yönteminin etkili olduğu söylenebilir.

Anahtar Kelimeler: Emülsifiye sıvı membran, ekstraksiyon, metilen bleu, modelleme, optimizasyon.

1. INTRODUCTION

Basic dye family represent the most important class of commercial dyes and are mainly used in textile, leather, paper, plastics, etc.[1-3]Among these dyes, methylene blue (MB) is a harmful pollutant and has been long been known for its detrimental effects on human health and the presence of low concentration improves water pollution.

The treatment and elimination of dyes from contaminated waters have been the subject of great attention in the last few years.[4] There are several methods for dyes removal such as adsorption,[5,6] extraction,[7] biological treatment, coagulation/flocculation, chemical oxidation and photocatalytic process etc.[8] Emulsion liquid membrane (ELM) has achieved a lot of attention seen in their advantages.[9]

DOI: http://dx.doi.org/10.32571/ijct.986667 **E-ISSN: 2602-277X**

The main objective of this work was to model and optimize the influence of various factors affecting the emulsion liquid membrane formation and its stability for removing MB. To achieve total elimination of dye, four factors such as the initial concentration of cationic dye (MB), the addition of salt (KCl/ NaCl/ Na_2SO_4), acid (HCl/ H_2SO_4/H_3PO_4) and the extractant concentration (10, 30 and 50 ppm) were followed applying a Box-Behnken design

The four parameters take each three levels according to the Box-Behnken design. The experiment matrix consists of 27 experiments. The Box-Behnken design makes it possible to minimize the number of experiences,[10-13] save time, money.

2. MATERIALS AND METHODS

2.1. Materials and compounds

Methylene bleu (MB) ($C_{16}H_{18}N_3ClS$) is a cationic dye supplied by Sigma Aldrich. The emulsified liquid membrane used for the extraction of MB consisted of monooleate of sorbitan (SPAN 80), an anionic commercial surfactant, di-2-ethylhexylphosphoric acid (D2EHPA) as the extractant, the fuel oil as the thinner. Sulfuric acid (95-97%, Fluka), phosphoric acid H_3PO_4 (85%, Merck), and hydrochloric acid HCl (37.25%, Merck) are the internal phase tested. The fuel oil used in this study is a fraction of Algerian petroleum. Demineralized water (pH=5.0–6.5) was used to prepare the external aqueous phase.

The addition of salt in the external aqueous phase was carried out. The salts used are sodium sulfate (Na_2SO_4) (99%, Merck), KCl (99%, Sigma-Aldrich), NaCl (99%, Sigma-Aldrich).

The homogenizer Moulinex active flow technology, with a capacity of 700 Whats was used to generate a stable emulsion for the extraction. Then, to ensure the dispersion of the emulsified membrane into a beaker containing the external aqueous phase, a mechanical stirrer type RW20 Kjank & Kunkel was used.

2.2. Methods

The ELM method consists to contact the aqueous phase containing the pollutant with an emulsion (W/O) which was formed of an organic phase (membrane) and an internal aqueous solution. Before extraction, a preliminary study of the ELM was essential to deduce the favorable conditions for the emulsion stability. The different parameters affecting the stability of membrane are the concentration of extractant, the concentration of internal phase, the time of emulsification, stirring speed, the ratio $V_{internal}$ / $V_{external}$ and $V_{externe}$/$V_{emulsion}$. The stability of the membrane has been verified in an interior study.[14] They found that the membrane is very stable. And the most favorable conditions for the stability of emulsified liquid membranes are: stirring speed = 200 rpm, SPAN 80 = 6%w, D2EHPA= 8 %w ; time of emulsification = 3 mn, ratio V_{Org}/V_{int} = 1, ratio $V_{internal}$ / $V_{external}$ = 5 and $[H_2SO_4]_{internal}$ = 1M.

The emulsion (W/O) was prepared by mixing two phases organic and aqueous with the homogenizer for three minutes (a time that is already optimized). The organic phase (membrane) consisted of SPAN 80, D2EHPA, and fuel oil. However, the aqueous phase was the acid. The emulsions are prepared according to the matrix given by the MINITAB 18.

The samples were analyzed using a visible spectrophotometer (PRIM-SECOMAM) (at 664nm) to determine the concentration of the residual MB. The extraction efficiency was calculated by equation (1).

$$R\% = [1 - \frac{[BM]_f}{[BM]_0}] \times 100 \qquad (1)$$

Where:
R : extraction yield (%).
$[MB]_f$: final concentration of MB in the external phase (ppm).
$[MB]_o$: initial concentration of MB in the external phase (ppm).

3. RESULTS AND DISCUSSION

3.1. Box-Behnken design

The industrial effluents are released into the aquatic environment loaded with various types of salts. In order to study the effect of the presence of salts in the solution, we have chosen three salts KCl, NaCl and Na_2SO_4 for levels (-1), (0) and (+1) respectively. The other factors studied are the weight percentage of D2EHPA (from 5 to 10% w), the initial concentration of MB dye (10 to 50ppm) and the type of acid in the internal phase (HCl (-1), H_2SO_4 (0) and H_3PO_4 (+1)). For this, an experimental design of second degree was envisaged (Table 1).

3.2. Anova

The ANOVA statistical analysis of experimental results are grouped in Table 2.

From the results of Table 2 it can be seen that the (internal phase) is a highly significant term on MB extraction with a p-value equal to zero. The linear effect and the square effect of the salt are significant terms where the value of the p-value is less than or equal to 0.05 (5%) with the values of p-value respectively equal to 0.05 and 0.03. We also observe that no interaction is significant.

DOI: http://dx.doi.org/10.32571/ijct.986667 **E-ISSN: 2602-277X**

Table.1: Experimental yields of MB extraction according to Box-Behnken design.

Essay	$[BM]_0$	Effect of salts	Internal phase	[D2EHPA]	R exp. %	R theo. %
1	30	KCl	H_2SO_4	5	98.98	99.79
2	50	NaCl	HCl	7.5	76.24	79.08
3	10	KCl	H_2SO_4	7.5	99.56	92.43
4	30	KCl	HCl	7.5	76.25	79.61
5	50	NaCl	H_3PO_4	7.5	82.32	77.59
6	30	NaCl	HCl	5	82.66	78.27
7	10	NaCl	HCl	7.5	61.34	70.16
8	30	NaCl	HCl	10	82.50	77.29
9	50	NaCl	H_2SO_4	5	99.07	98.34
10	30	Na_2SO_4	HCl	7.5	92.48	87.05
11	50	KCl	H_2SO_4	7.5	96.75	94.86
12	50	Na_2SO_4	H_2SO_4	7.5	99.81	102.00
13	30	NaCl	H_2SO_4	7.5	96.26	93.54
14	10	Na_2SO_4	H_2SO_4	7.5	100.00	98.56
15	10	NaCl	H_2SO_4	10	91.25	92.11
16	30	KCl	H_2SO_4	10	94.55	93.81
17	30	Na_2SO_4	H_2SO_4	5	98.90	103.00
18	50	NaCl	H_2SO_4	10	86.43	88.07
19	30	Na_2SO_4	H_3PO_4	7.5	93.99	90.75
20	30	KCl	H_3PO_4	7.5	78.67	84.24
21	30	NaCl	H_3PO_4	5	83.43	84.40
22	30	NaCl	H_2SO_4	7.5	94.08	93.54
23	10	NaCl	H_2SO_4	5	89.29	87.77
24	30	NaCl	H_3PO_4	10	79.30	79.46
25	30	Na_2SO_4	H_2SO_4	10	100.00	103.00
26	10	NaCl	H_3PO_4	7.5	78.71	79.97
27	30	NaCl	H_2SO_4	7.5	90.28	93.54

Table.2 : Estimated coefficients for the yield of MB extraction for coded units.

Terms	**Coef**	**SE Coef**	**T**	**P**
Constant	93.54	3.19	29.29	0.000
$[BM]_0$	1.64	1.60	1.02	0.33
Salts	3.49	1.60	2.18	**0.05**
internal Phase (Acids)	2.08	1.60	1.30	0.22
D2EHPA	-1.48	1.60	-0.93	0.37
$[BM]_0{}^2$	-2.56	2.40	-1.07	0.31
$(Salts)^2$	6.15	2.40	2.57	**0.03**
$(internal\ phase)^2$	-14.28	2.40	-5.96	**0.000**
$(D2EHPA)^2$	0.59	2.40	0.25	0.81
$[BM]_0$× salts	0.42	2.77	0.15	0.88
$[BM]_0$ × internal phase	-2.82	2.77	-1.02	0.33
$[BM]_0$× (D2EHPA)	-3.65	2.77	-1.32	0.21
Salts× internal phase	-0.23	2.77	-0.08	0.94
Salts×(D2EHPA)	1.51	2.77	0.55	0.60
internal Phase ×(D2EHPA)	-0.99	2.77	-0.36	0.73

DOI: http://dx.doi.org/10.32571/ijct.986667 E-ISSN: 2602-277X

3.3. Mathematical model

The mathematical model is a second degree and relates the extraction yield to the different factors, their squares and their interactions. For coded units the model is represented by equation 2:

$$\mathbf{R(\%)} = 93.5420 - 1.6353 \times \mathbf{[BM]_0} - 3.4873 \times \mathbf{(salt)} - 2.0793 \times \mathbf{(internal\ phase)} + 1.4818 \times \mathbf{(Extractant)} + 2.5611 \times \mathbf{[BM]_0^2} - 6.1477 \times \mathbf{(salt)^2} + 14.2781 \times \mathbf{(internal\ phase)^2} - 0.5935 \times \mathbf{(Extractant)^2} - 0.4216 \times \mathbf{[BM]_0 \times (salt)} + 2.8231 \times \mathbf{[BM]_0 \times (internal\ phase)} + 3.6508 \times \mathbf{[BM]_0} \times \mathbf{(Extractant)} + 0.2315 \times \mathbf{(salt)} \times \mathbf{(internal\ phase)} - 1.5076 \times \mathbf{(salt) \times (Extractant)} - 0.9902 \times \mathbf{(internal\ Phase) \times (Extractant)} \quad (2)$$

3.4. Effects of factors

A factor may be a qualitative or quantitative variable, continuous or discontinuous, controllable or uncontrollable.[15] Figure 1 shows the effect of the factors studied in the chosen domain on the yield of MB extraction.

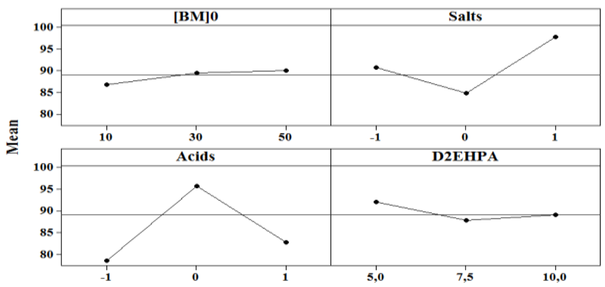

Figure1. Effects of factors.

Two effects are observed; the first is a negative effect of 5 to 7.5% by mass and a second positive effect of 7.5 to 10% by mass (with a weak slope). It can be said that the yield is good at a minimum level of the mass percentage of extractant. This is explained with a high mass percentage extractant (D2EHPA) the membrane becomes a little viscous, which means that the transfer is difficult.[16]

It is observed that there are two slopes, a negative one from KCl (-1) to NaCl and a positive slope from NaCl to Na_2SO_4. Therefore, we can say that the presence of Na_2SO_4 promotes the extraction of methylene blue which it has been obtained a yield of 97.76%. It was observed that there is a positive effect from HCl to H_2SO_4 and a negative effect from H_2SO_4 to H_3PO_4. It was also found that the H_2SO_4 acid gives the best removal efficiency (95.77%) of methylene blue dye. So, we can explain this result by the presence of hydrogen ions ($2H^+$) which promotes the discoloration of aqueous solutions of MB.[17] It was observed that there is a positive effect of the initial dye concentration with a moderately high slope (low inclination). It was found that increasing the dye concentration increases the yield of the dye extraction (from 86.83 to 90.10%). Therefore, the concentration of 50 ppm in methylene blue gives the best result.[18,19]

3.5. Henry's line of residual values

Generally, Henry's line is useful for checking the normality of the model. We see that the points tend to form a line.

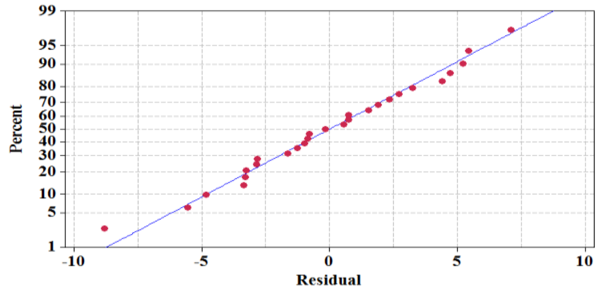

Figure 2. Henry's right of residual values for yield.

3.6. Graphics contour and surface responses

At an initial concentration of $[BM]_0$ equal to 50 ppm and in the presence of Na_2SO_4, it can be seen that the good yields are of the order of 100% in an average level for the acid (internal phase is sulfuric acid H_2SO_4) and at a concentration of minimum value of D2EHPA (5% m). The response surface is convex, giving the same findings of the contour.

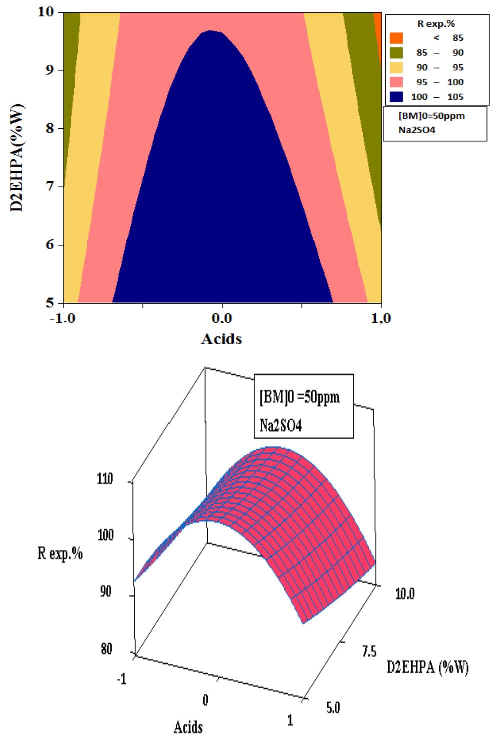

Figure 3. Graphic contour and surface responses as function of acid-D2EHPA with $[BM]_0$ = 50 ppm and Na_2SO_4 salt.

DOI: http://dx.doi.org/10.32571/ijct.986667 E-ISSN: 2602-277X

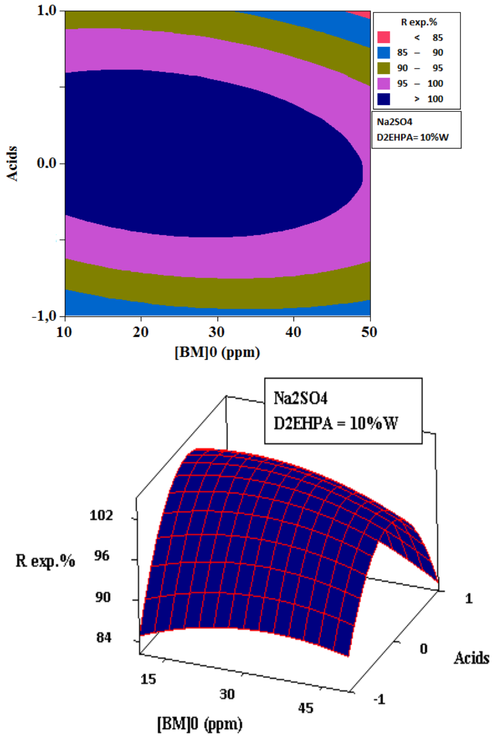

Figure 4. Graphic response contour as a function of $[BM]_0$ - acids with salt Na_2SO_4 and D2EHPA = 10% m.

By fixing the salt Na_2SO_4 and the mass percentage of D2EHPA at 10% m, it is noted that the good yields take a large place in the contour surface under the conditions $[BM]_0$ of (10ppm-50ppm) and in the presence of the phase internal H_2SO_4. The response surface indicates the same observations

3.7. Experimental yield depending on the theoretical yield

From Figure.5 it can be seen that the experimental and estimated yields are distributed around the regression line (R^2 = 0.9553). The fit is very good, especially above 80%.

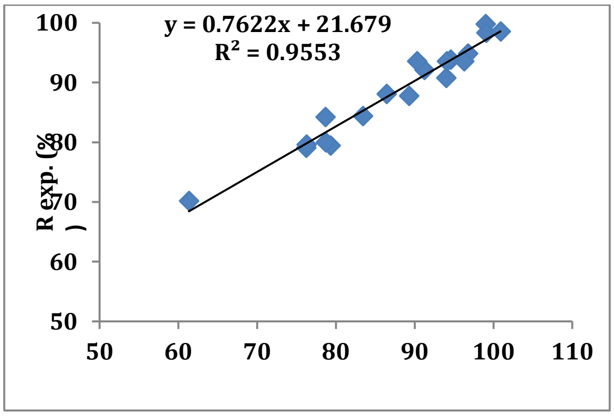

Figure 5. Graphical representation of measured responses as function of theoretical responses for BM extraction.

4. OPTIMISATION

The goal is to maximize the extraction yield. A constraint was imposed on studied factors. The best elimination of MB dye is obtained under optimal conditions: 30 ppm for the initial concentration of $[BM]_0$, 10%w for the extracting (D2EHPA) with the presence of Na_2SO_4 and H_2SO_4.

Finally, we can say that in total we could extract the entire MB using the emulsified liquid membrane technique.

5. CONCLUSIONS

The elimination of the cationic pollutant "methylene blue" is influenced by several factors that have demonstrated the possibility of using the emulsified liquid membrane extraction process.

A membrane consists of a surfactant (span80), a diluent (fuel oil) and an extractant (D2EHPA) in the organic phase, varying the type of acids as an internal phase. In addition, an external aqueous phase of the MB dye mixture with salt at different concentrations of pollutant (MB) has been studied in order to find the optimal conditions that promote the extraction yield of the cationic dye MB.

From the Box-Behnken design, we obtained several information which increase the experimental yield of MB extraction. Thus, after optimizing the extraction of MB, we found the best optimal conditions, which are: a weight percentage of extractant equal to 10%w, the presence of sulfuric acid as the internal phase, the initial concentration of dye is 30 ppm, the salt that promotes extraction is Na_2SO_4 for total extraction of MB.

ACKNOWLEDGEMENTS

We thank Prof. Abbes Boukhari Director of the LOMOP Research Laboratory and Dr Fethi Saoudi Head of the Process Engineering Department, BadjMokhtar University of Annaba, for providing us with the necessary material resources.

Conflict of interests

I declares that there is no a conflict of interest with any person, institute, company, etc.

REFERENCES

1. R.S. Juang et al., *Environ. Technol.*, **1997**, 18, 525- 531.

2. C Zaharia, D Suteu. Textile organic dyes – characteristics polluting effects and sep-aration/elimination procedures from industrial effluents –

DOI: http://dx.doi.org/10.32571/ijct.986667 E-ISSN: 2602-277X

a critical overview or-ganic pollutants ten years after the Stockholm convention - environmental and analytical update. In: Puzyn T, editor. Croatia: Tech Europr; **2012**.

3. M. Djenouhat et al., *Royal Society Open Science*, **2018**, 5: 171220.

4. H. Ghodbane et al., *Ultrason. Sonochem*. 16 (**2009**) 593–598.

5. El-Khamssa. Guechi et al., *Desalination and water treatment*, **2012**, Volume 38, issue 1-3, pp. 401-408.

6. L. Bouziane et al., *Desalination and water treatment*, **2012**, Volume 49, issue 1-3,189-199.

7. F. Bendebane e al., *Poll Res*., **2016**, 35(4): 23-29, ISSN 0257–8050.

8. L. Bahloul et al., *Journal of Taiwan Institute of Chemical Engineers*, **2016**, Volume-59, page 26-32, Issue-7.

9. EA. Fouad et al., *Journal of Membrane Science*, **2008**, Vol. 307, p. 156–168.

10. J-J. Droesbeke, J. Fine, G. Saporta, Plans d'expériences, applications à l'entreprise, association pour la statistique et ses utilisations. société statistique de France, éditions Techni, pp509, chapitre 2, Paris; **1997**.

11. P. Dangnelie, Principes d'expérimentation, Gembloux, Presses Agronomiques; **1993**.

12. P. Dangnelie, Statistique théorique et appliquée, Tome 1 : Les bases théoriques, Gembloux, Presses Agronomiques; **1992**.

13. J. Mare-Azaïs, Composantes de la variabilité des plans d'expériences. laboratoire de statistique et probabilité-UMR CNRS C55830. Université Paul Sabatier-31062-Toulouse Cedex 4.

14. I. Amirat, Elimination du colorant cationique (BM) par les membranes liquides émulsionnée, application des plans d'expériences, mémoire de Master, université Badji Mokhtar –Annaba; **2016**.

15. J. Goupy, Plans d'expériences, Techniques de l'ingénieur, traité Analyse et Caractérisation, Volume PE 230, 1-28 **1998**.

16. M. Djenouhat et *al*, *Separation and purification Technology*, **2008**, 63 : 231-238.

17. M. Lechheb, extraction du colorant orange II en milieu aqueux par membrane liquide émulsionnée, Université Badji Mokhtar Annaba; **2016**.

18. A. Kargari et al., *Desalination*, **2004**, 162, 237-247.

19. J-Q. Shen et al., *Journal of Membrane Science*, **1996**, 120: 45-53.