# Supplementary information - Removal of estrogens from aqueous solutions using 3D printed polymer scavengers

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## Table 1 Hormone characteristics

	Molecular weight (mol/g)	CAS Number	Log P	Solubility in H <sub>2</sub> O
Estrone (E1)	270.37	53-16-7	2.6	1.3 mg/L at 25 °C[1]
$17\beta$ -estradiol (E2)	272.38	50-28-2	4.01	1.5 mg/L at 25 °C[1]
Estriol (E3)	288.38	50-27-1	2.45	-
$17\alpha$ -ethinylestradiol (EE2)	296.40	57-63-6	3.67	9.2 mg/L at 25 °C [1]

#### Table 2 Printing parameters used with different materials

Polymer	Polyurethane TPU/PU	Polyamide-12 PA12	Polypropylene PP	Polystyrene PS	30 % Activated carbon with polyamide-12 ACPA12
Laser power (W)	7	4.2	7	14	5.6
Scan speed (mm/s)	1600	2560	2560	1600	2000
Powder bed temperature (°C)	119	172	132	99	172
Energy density (mJ/mm <sup>2</sup> )	17.5	6.6	11	35	11.2
Filter weight (g)	$0.7\pm0.1$	$0.5\pm0.1$	$0.6\pm0.1$	$0.5\pm0.1$	$0.6\pm0.1$
Hatching space, hs (mm)	0.25	0.25	0.25	0.25	0.25
Layer thickness (mm)	0.1	0.1	0.1	0.1	0.1

#### Table 3 Mass Spectrometer settings

	Precursor ion (m/z)	Fragment ions (m/z)	Collision energy (eV)	Fragmentor voltage (V)	Retention time (min)	ESI mode
Estrone (E1)	269	145/143	40/45	170	6.488	negative
$17\beta$ -estradiol (E2)	271	183/145	45/45	170	6.276	negative
Estriol (E3)	287	171/145	45/45	170	4.184	negative
17 $\alpha$ -ethinylestradiol (EE2)	295	145/143	45/45	170	6.423	negative

#### Table 4 Elution studies

Polymer	Mode	Hormone	Value (%)	SD
PA12	Elution	E1	124.096	58.998
PA12	Elution	E2	77.805	16.264
PA12	Elution	E3	32.515	31.554
PA12	Elution	EE2	98.382	27.059
PA12	Recovery	E1	51.68	9.166
PA12	Recovery	E2	68.782	8.557
PA12	Recovery	E3	13.869	11.267
PA12	Recovery	EE2	79.975	10.626
PA12	Wash	E1	18.153	13.95
PA12	Wash	E2	8.513	9.124
PA12	Wash	E3	3.269	5.662
PA12	Wash	EE2	8.023	8.96
TPU	Elution	E1	84.403	7.737
TPU	Elution	E2	99.125	14.921
TPU	Elution	E3	72.211	14.21
TPU	Elution	EE2	25.62	10.805
TPU	Recovery	E1	72.636	5.611
TPU	Recovery	E2	81.041	7.721
TPU	Recovery	E3	74.711	7.877
TPU	Recovery	EE2	38.605	5.171
TPU	Wash	E1	12.572	0.97
TPU	Wash	E2	1.5	0.511
TPU	Wash	E3	1.585	0.55
TPU	Wash	EE2	1.315	2.223
ACPA	Elution	E1	0	0
ACPA	Elution	E2	0	0
ACPA	Elution	E3	2.666	1.225
ACPA	Elution	EE2	7.082	0.648
ACPA	Recovery	E1	100	0
ACPA	Recovery	E2	100	0
ACPA	Recovery	E3	100	0
ACPA	Recovery	EE2	100	0
ACPA	Wash	E1	0	0
ACPA	Wash	E2	0	0
ACPA	Wash	E3	0	0
ACPA	Wash	EE2	0	0

Estrogen								
Models	RMSE	MAE	MSE	RAE	AIC	BIC	R2	SE
Elovich	0.001091	0.000799	0.000001	0.099446	-80.4239	-80.1856	0.9857981	0.001260
FractionalPower	0.123901	0.096434	0.015351	0.211603	-4.7093	-4.4710	0.9465547	0.143069
PFO	0.644463	0.520187	0.415333	0.518165	19.6736	19.8325	0.8971858	0.744162
PSO	35.684298	24.164207	1273.369111	0.050631	83.8984	84.0573	0.9961085	41.204678
Models	Parameter1		Parameter2					
Elovich	alpha	154.289279	beta	151.489978				
FractionalPower	alpha	0.243317	beta	0.378586				
PFO	k.PFO	0.066130	qe*	0.03206093				
PSO	k.PSO	7.799962	qe*	0.033463				
17B-estradiol								
Models	RMSE	MAE	MSE	RAE	AIC	BIC	R2	SE
Elovich	0.001484	0.001232	0.00002	0.215970	-75.5012	-75.2629	0.9541579	0.001714
FractionalPower	0.136281	0.112926	0.018573	0.400100	-3.1855	-2.9472	0.8627716	0.157364
PFO	0.501286	0.424803	0.251287	0.453906	15.6537	15.8126	0.9490361	0.578835
PSO	18.219800	14,984765	331.961120	0.031436	73,1432	73.3020	0.9988456	21.038413
Models	Parameter1	1 11/0 1/ 00	Parameter2	01001100	/ 011 102	,010020		11000 110
Elovich	alpha	211,761899	beta	199.266298				
FractionalPower	alpha	0 398520	beta	0 253226				
PFO	k PFO	0.082277	de*	0.03203200				
PSO	k.PSO	14.427932	qe*	0.0331483				
Estriol	DIAGE	1445	MOD	DAE		DIG	PO	0.77
Models	RMSE	MAE	MSE	RAE	AIC	BIC	R2	SE
Elovich	0.000238	0.000203	0.000000e+00	0.318102	-104.7880	-104.5497	0.8902929	0.000275
FractionalPower	NA	NA	NA	NA	-Inf	-Inf	NA	NA
PFO	0.304886	0.271649	9.295600e-02	0.437691	7.6979	7.8568	0.9466665	0.352052
PSO	68711.048138	58749.288245	4.721208e+09	5.385627	204.9057	205.0645	-16.4589388	79340.684278
Models	Parameter1		Parameter2					
Elovich	alpha	-1664.627091	beta	-1664.896423				
FractionalPower	alpha	0.314456	beta	-				
PFO	k.PFO	-0.038025	qe*	0.0002342073				
PSO	k.PSO	-85.229624	qe*	0.00017884				
$17\alpha$ -ethinylestradiol								
Models	RMSE	MAE	MSE	RAE	AIC	BIC	R2	SE
Elovich	0.001495	0.001237	0.00002	0.176030	-75.3844	-75,1461	0.9686455	0.001727
FractionalPower	0.142140	0.116487	0.020204	0.369343	-2.5120	-2.2737	0.8773928	0.164130
PFO	0.434088	0.362254	0.188432	0.452049	13.3509	13.5098	0.9490007	0.501241
PSO	22.222057	18.479084	493.819834	0.044786	76.3204	76.4793	0.9976729	25.659822
Models	Parameter1		Parameter2		,			
Elovich	alpha	170,481407	beta	162.371084				
FractionalPower	alpha	0 349874	beta	0 281775				
PFO	k PFO	0.071222	ne*	0.03825916				
PSO	k PSO	8 863876	ч~ ле*	0.0395209				
		0.000070	7~	0.00/020/				

Table 5 Linear Adsorption Kinetic Models Obtained Using R Version 4.1.1 and PUPAK 0.1.1

\*  $\boldsymbol{q}_{e}$  values have been calculated using last  $\boldsymbol{q}_{t}$  and t of the run.

Estragon							
Models	DMCE	MAE	MSE	DAF	AIC	BIC	<b>SE</b>
DEO	1.971400- 02	1 6602610 02	2 5021200 06	2.050040- 01	0 1510240 + 01	<u> 002666a + 01</u>	2 121069 02
Pro DSO	0.7924250.04	2 260207o 04	0 5606020 07	2.0509400-01	$-0.1310340\pm01$	$-6.0920000\pm01$	2.1219060-03
Models	9.702433E-04 Doromotor1	0.0093976-04	9.309003E-07	1.09032/6-01	-9.3194040701	-9.20029/0701	1.1092246-03
DEO	1-1	0 1 5 4 7 6 9	Falaineteiz	0.021202			
Pro DCO	K1 1-0	0.154/00	qe	0.031202			
P30	KΖ	5.000/105	qe	0.0352/00			
$17\beta$ -estradiol							
Models	RMSE	MAE	MSE	RAE	AIC	BIC	SE
PFO	1.998561e-03	1.744994e-03	3.994247e-06	3.092966e-01	-8.033500e+01	-7.974333e+01	2.266156e-03
PSO	9.995683e-04	8.639873e-04	9.991368e-07	1.531400e-01	-9.280647e+01	-9.221480e+01	1.133404e-03
Models	Parameter1		Parameter2				
PFO	k1	0.3730920	qe	0.0294744			
PSO	k2	15.82	qe	0.03186			
Estriol							
Models	RMSE	MAE	MSE	RAE	AIC	BIC	SE
PFO	1.436015e-04	8.940745e-05	2.062140e-08	1.293446e-01	-1.277315e+02	-1.271399e+02	1.628288e-04
PSO	1.436019e-04	8.940601e-05	2.062150e-08	1.293425e-01	-1.277315e+02	-1.271398e+02	1.628292e-04
Models	Parameter1		Parameter2				
PFO	k1	-0.0004597	qe	0.0738999			
PSO	k2	-0.001506	qe	0.150182			
$17\alpha$ -ethinylestradiol							
Models	RMSE	MAE	MSE	RAE	AIC	BIC	SE
PFO	2.625442e-03	2.350611e-03	6.892945e-06	3.344919e-01	-7.542422e+01	-7.483254e+01	2.976971e-03
PSO	1.426566e-03	1.218023e-03	2.035089e-06	1.733247e-01	-8.640384e+01	-8.581217e+01	1.617573e-03
Models	Parameter1		Parameter2				
PFO	k1	0.309740	qe	0.033960			
PSO	k2	11.03	qe	0.03706			

Table 6 Non-Linear Adsorption Kinetic Models Obtained Using R Version 4.1.1 and PUPAK 0.1.1



Fig. 1 Generic chemical structure of polyurethane modified from Sánchez-Calderón, I. et al. (2021)[2]



Fig. 2 Generic chemical structure of polyamide-12 modified from Klein (2018)[3]

## 1 References

1. Shareef A. et al. Aqueous Solubilities of Estrone,  $17\beta$ -Estradiol,  $17\alpha$ -Ethynylestradiol, and Bisphenol A. Journal of Chemical and Engineering Data - J CHEM ENG DATA. 51. (2006) 10.1021/je050318c.

2. Sánchez-Calderón, I. et al. Effect of the Molecular Structure of TPU on the Cellular Structure of Nanocellular Polymers Based on PMMA/TPU Blends. Polymers 13, 3055 (2021)

3. Klein, J. P. Methods and compounds for producing nylon 12. US Patent 9,994,677 B2 (2018).