An enquiry on appropriate selection of polymers for preparation of polymeric nanosorbents and nanofiltration/ultrafiltration membranes for hormone micropollutants removal from water effluents

Abstract

To analyze polymeric nanosorbents and nanofiltration/ultrafiltration membranes for hormone micropollutants removal from water effluents, here an in-through investigation on the suitability and compatibility of various polymers has been carried out. For this work, estradiol, estrone, testosterone, progesterone, estriol, mestranol, and ethinylestradiol were considered. A total number of 452 polymers were analyzed and initially screened using Hansen solubility parameters. The identified good pairs of hormones and polymers then were examined to obtain the equilibrium capacity of hormones removal from water effluents using a modified Flory–Huggins model. A distribution coefficient was defined as the ratio of hormones in water effluent phase and polymer phase. For removal of mestranol, estradiol and ethinylestradiol, no compatible polymer was identified based on initial screening of collected database. Three compatible polymers were identified for estriol. For progesterone, a wide variety of polymers was identified as good matching of polar, dispersion and hydrogen forces contributions can be observed for these pairs. For estrone, only two polymers can be proposed due to the mismatch observed between polar, dispersion and hydrogen forces contributions of other polymers and this hormone. The phase calculations showed that not all the identified good pairs could be used for practical separation applications. The domain of applicability of each good pair was investigated and potential polymers for practical micropollutants removal together with their removal capacity were represented in terms of phase envelops. The theoretical approach follows fundamental chemical thermodynamic equations and then can be simply applied for any system of interest.

Keywords: hormones micropollutants; sorption; polymers; Hansen parameter; phase envelops

# Introduction

The increasing micropollutants content of water due to environmental pollution and pollutants originating in human activity and sources might cause serious health and ecosystem issues [[1-5](#_ENREF_1)]. A significant amount of pesticides, pharmaceuticals, personal care products, plasticizers, antibiotics, hormones, endocrine disrupters and other organic contaminates have been detected in water effluents [[6-11](#_ENREF_6)]. So, to remove these micropollutants from water effluents, various treatment technologies have been developed such as activated carbon adsorption, coagulation, oxidation, membrane-based technology as reported in literature [[12](#_ENREF_12),[11](#_ENREF_11),[13](#_ENREF_13)].

These technologies have been examined against efficiency and applicability through experimental works in laboratory and pilot scales. Assessments showed that activated carbon adsorption and coagulation technologies are not effective, and oxidation technique produces by-products that might be toxic [[14](#_ENREF_14)]. The application of the membrane technology revealed that nanofiltration and reverse osmosis membranes have high potential to remove micropollutants [[15](#_ENREF_15),[16](#_ENREF_16)]. Sorption of micropollutants in polymeric materials used in membranes plays an important role for reliability and versatility of water treatments [[15](#_ENREF_15),[16](#_ENREF_16)]. The choice of raw polymer is therefore, the key step for micropollutants removal using polymeric membranes.

Noting that almost all of the used membranes are tailored and evaluated eventually in a trial-and-error manner, thus, it is a required need to develop a method for feasibility analysis and design to provide a general guideline on how these polymeric membranes, and as a side the polymeric nanosorbents, must be selected. As there are many different types of contaminants available in water, the effect of each contaminant, in a quantitative manner, can be evaluated using multi component liquid-liquid equilibrium and sorption studies; however, the large number of contaminants is an issue for such study. Therefore, in present work, as an in-through analysis, a feasibility and selection study is provided for the optimal selection of raw materials to reduce the costly and time consuming process of nanosorbents and membranes and their individual evaluation. To identify the appropriate polymeric materials, the fundamental chemical thermodynamic equations and relationships are followed.

A total number of 452 polymers were analyzed and initially screened for compatibility using Hansen solubility parameter. Then, for pairs which are identified as “good”, the removal equilibrium capacity of hormones from water effluents was determined using a Flory–Huggins model based on the Hansen solubility parameters and the results were reported in the form of phase envelop.

# Method of evaluations

In various industries, for solvent selection, predicting compatibility of polymers and etc., Hansen solubility parameters have been used [[17](#_ENREF_17),[18](#_ENREF_18)]. The solubility parameter () has been defined based on regular solution theory of Hildebrand and divided into divided into three contributions namely; (1) non-polar (dispersion) forces (), (2) polar forces () and (3) hydrogen-bonding effects () as given by Eq. 1 [[17](#_ENREF_17)];

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| --- | --- |
|  | 1 |

Two compounds are compatible provided that the difference between their solubility parameters is small and their solubility parameters are relatively close to each other. Having compound 1, in order to find compatible compounds 2, at first two objectives *R0* and *R1* can be defined as given in Eqs. 2-3 [[18](#_ENREF_18)] where subscript 1 denotes to compound 1 for which compatibility of other compounds is being checked.

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| --- | --- |
|  | 2 |
|  | 3 |

A second compound (2) is highly compatible to compound 1, if following objectives are being satisfied [[18](#_ENREF_18)].

|  |  |
| --- | --- |
|  | 4 |
|  | 5 |

A second compound (2) is poorly compatible to compound 1, if following objectives are being satisfied [[18](#_ENREF_18)].

|  |  |
| --- | --- |
|  | 6 |
|  | 7 |

A second compound (2) is incompatible to compound 1, if following objectives are being satisfied [[18](#_ENREF_18)].

|  |  |
| --- | --- |
|  | 8 |
|  | 9 |

Using these criteria, the compatible compound pairs can be found.

Therefore, the collected database of 452 polymers was analyzed against their compatibility for each considered hormones and potential compatible pairs were analyzed for the equilibrium removal capacity following fundamental chemical thermodynamic equations [[19](#_ENREF_19)].

By contacting the water effluent containing hormones to the polymers, a local thermodynamic equilibrium will be established at the interface of these two phases. In each case, the chemical potentials of hormones in two contacting phases must be equal [[19](#_ENREF_19)] at the operating conditions i.e. temperature (*T*) and pressure (*P*) as given by Eq. 10.

Superscript *w* and *p* respectively accounts for water and polymer phases. Subscript 1 denotes the hormones of interest. *μ* denotes the chemical potential and Δ accounts for the change in chemical potential referring to a reference state [[19](#_ENREF_19)].

|  |  |
| --- | --- |
|  | 10 |

Eq. 10 can be rewritten as given by Eq. 11 by employing the same reference state for both phases [[19](#_ENREF_19)], where *x* and γ denote the mole fraction and the activity coefficient of hormones of interest respectively.

|  |  |
| --- | --- |
|  | 11 |

For calculation of activity coefficient, a Flory–Huggins model based on the Hansen solubility parameters was used here which for binary mixtures is given by Eq. 12 [[17](#_ENREF_17)] where  and  are the volume fractions and mole fractions and  is the composition independent Flory–Huggins interaction parameter between compound 1 (hormones) and compound 2 (polymer) which is given by Eq. 13 [[17](#_ENREF_17)] where *V1* is molar volume of compound 1 (hormones), *R* is the universal gas constant and *T* is the temperature.

|  |  |
| --- | --- |
|  | 12 |
|  | 13 |

Using Eq. 12, one might write Eq. 14;

|  |  |
| --- | --- |
|  | 14 |

Thus, for sorption onto polymers, Eq. 11 reads Eq. 15;

|  |  |
| --- | --- |
|  | 15 |

One might write, thus, Eq. 15 simplifies to Eq. 16;

|  |  |
| --- | --- |
|  | 16 |

The removal/separation performance of polymers can be practically evaluated by defining a distribution coefficient as  where superscript *w* and *p* respectively accounts for water and polymer phases. A distribution coefficient larger than 1 is of much interest as it implies that the hormones content of polymers is much more than that in water.

Eq. 16 can be simplified by inserting this distribution coefficient which read Eq. 17;

|  |  |
| --- | --- |
|  | 17 |

This equation (Eq. 17) is of practical interest as for each water sample with hormones content of, using an iterative root seeking method; the distribution coefficients can be calculated. Then, the hormones content in polymers can be calculated as .

# Result and discussion

A database of 452 polymers was collected from Ref. [[18](#_ENREF_18)] and is provided as *supplementary file*. The calculated solubility parameters of studied hormones are listed in Table 1. The calculated values of Δa=|δa,1-δa,2| for each polymer-hormone pairs are listed in *supplementary file* also.

Table 1. The calculated solubility parameters of studied hormones

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| No. | Hormones | Dispersion  (MPa0.5) | Polar  (MPa0.5) | Hydrogen Bonding  (MPa0.5) | Molar Volume  (cm3/mol) |
| 1 | Estradiol | 19.87 | 4.72 | 13.74 | 211.83 |
| 2 | Estrone | 18.48 | 3.96 | 9.74 | 232.10 |
| 3 | Testosterone | 18.51 | 3.61 | 9.30 | 254.50 |
| 4 | Progesterone | 19.68 | 5.73 | 3.86 | 268.77 |
| 5 | Estriol | 18.90 | 6.53 | 16.17 | 229.6 |
| 6 | Mestranol | 18.50 | 2.62 | 9.70 | 244.30 |
| 7 | Ethinylestradiol | 17.45 | 4.14 | 12.88 | 241.30 |

Using Eqs. 2-3, values of the two objectives *R0* and *R1* were determined and summarized in Table 2.

Table 2. The values of the two objectives *R0* and *R1*

|  |  |  |  |
| --- | --- | --- | --- |
| No. | Hormones | *R1* | *R0* |
| 1 | Estradiol | 6.69 | 0.55 |
| 2 | Estrone | 9.17 | 0.42 |
| 3 | Testosterone | 9.56 | 0.35 |
| 4 | Progesterone | 16.64 | 0.82 |
| 5 | Estriol | 3.83 | 1.10 |
| 6 | Mestranol | 8.98 | 0.18 |
| 7 | Ethinylestradiol | 5.06 | 0.49 |

Based on the initial Hansen solubility parameter screening, for the removal of hormone systems No. 1 (estradiol), No. 6 (mestranol) and No. 7 (ethinylestradiol), sorption in polymers cannot be recommended as no high compatible pair was identified. This is due to considerable differences in three Hansen solubility parameters which results in a mismatch in possible polar, dispersion and hydrogen forces contributions and reduce the solubility and compatibility. For hormone system No. 4 (progesterone), a wide variety of options are available for sorption onto polymers including polymers No. 41 (chloropar 40), No.72 (vilit mc 39), No.78 (v-lite vyhh), No.83 (alf an 950), No. 92 (soalk 1935-egax), No. 93 (vest-it bl908), No. 111 (den 444), No. 180 (pp), No. 190 (pbutylacrylate), No. 301 (elvax eod 3602-1) and No. 439 (lumflon lf200 30). The values of Δa=|δa,1-δa,2| for these polymers and progesterone are small indicating a good matching of polar, dispersion and hydrogen forces contributions and higher compatibility. For hormone system No. 2 (estrone), two polymer systems can be proposed for sorption namely; polymer No. 386 (r q silicone 748) and No. 254 (deg isoph). Due to the mismatch observed between polar, dispersion and hydrogen forces contributions of other polymers and this hormone, the only these two polymers are advised. Only polymer No. 136 (vit 4 h) can be used for sorption removal of hormone No. 3 (testosterone) as demonstrated by the desirable matching of Hansen solubility parameters. For hormone system No. 5 (estriol), polymers No. 102 (synr a 560), No. 112 (zink silicate (cr)) and No. 245 (mma/ea/an 40/40/20) are the available options for sorption removal.

For equilibrium removal capacity of optimal pairs identified in previous step, to perform the calculation using Eq. 17, at first, it is required to evaluate the interaction parameters, χ12. The calculated interaction parameters are listed in Table 3 for each hormone-polymer pair.

Table 3. The calculated values of χ12for polymers (system numbers as listed in Table 4)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| No. | Estrone | Testosterone | Progesterone | Estriol |
| 41 | 0.36 | 0.42 | 0.79 | 1.17 |
| 72 | 0.32 | 0.35 | 0.29 | 1.28 |
| 78 | 0.82 | 0.92 | 0.73 | 1.78 |
| 83 | 2.35 | 2.65 | 1.91 | 2.40 |
| 92 | 0.85 | 1.01 | 1.09 | 1.22 |
| 93 | 1.11 | 1.26 | 0.76 | 1.85 |
| 102 | 0.79 | 0.89 | 1.29 | 0.93 |
| 111 | 0.88 | 1.04 | 1.04 | 1.03 |
| 112 | 4.69 | 5.37 | 5.93 | 2.85 |
| 136 | 3.20 | 3.64 | 4.29 | 3.45 |
| 180 | 1.31 | 1.28 | 0.85 | 3.84 |
| 190 | 1.29 | 1.39 | 0.97 | 2.90 |
| 245 | 1.43 | 1.68 | 1.77 | 1.12 |
| 301 | 0.74 | 0.71 | 0.37 | 2.75 |
| 386 | 2.27 | 2.41 | 2.37 | 4.59 |
| 439 | 0.75 | 0.74 | 0.05 | 2.48 |

In Fig. 1(a) the results of equilibrium calculations for sorption of estrone onto polymer No. 112 (zink silicate (cr)) are shown. It can be seen that for volume fraction of estrone in water in the range of 0.4 up to 0.92, a miscibility gap exists denoting that for each volume faction of estrone in water, two different compositions in polymer can be distinguished indicating the occurrence of a phase separation. It can be seen that upon phase separation, nearly highly pure estrone separated regions can be obtained. In Fig. 1(b), the results of equilibrium calculations for sorption of estrone onto polymer No. 136 (vit 4 h) are shown. It can be seen that for volume fraction of estrone in water in the range of 0.63 up to 0.98, a miscibility gap exists denoting that for each volume faction of estrone in water, two different compositions in polymer can be distinguished indicating the occurrence of a phase separation. Here, estrone separated regions of about 70% purity can be obtained.

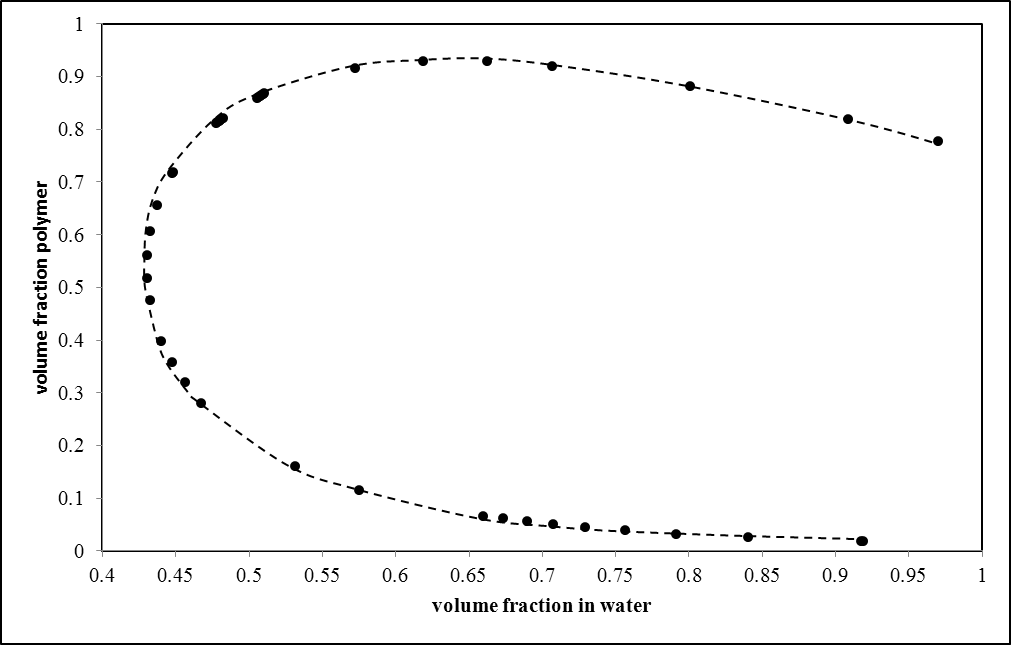


Fig. 1(a). Phase envelope for polymer No. 112 (zink silicate (cr)) and hormone No. 2 (estrone): bullets denote calculated points and dash line shows fit

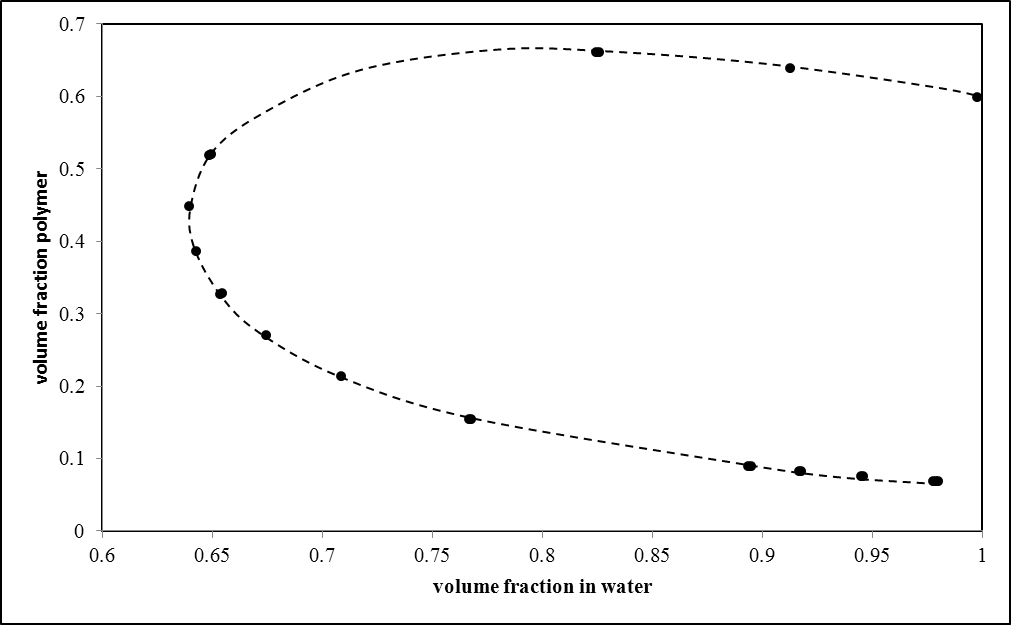


Fig. 1(b). Phase envelope for polymer No. 136 (vit 4 h) and hormone No. 2 (estrone): bullets denote calculated points and dash line shows fit

In Fig. 2(a), the results of equilibrium calculations for sorption of testosterone onto polymer No. 83 (alf an 950) are shown. It can be seen that for volume fraction of testosterone in water in the range of beyond 0.82, a miscibility gap exists denoting that for each volume faction of testosterone in water, two different compositions in polymer can be distinguished indicating the occurrence of a phase separation. The testosterone separated regions have no more than 50% purity, so this polymer cannot be advised to be used for practical testosterone treatment. In Fig. 2(b), the results of equilibrium calculations for sorption of testosterone onto polymer No. 112 (zink silicate (CR)) are shown. It can be seen that for volume fraction of testosterone in water in the range of 0.35 up to 0.85, a miscibility gap exists denoting that for each volume faction of testosterone in water, two different compositions in polymer can be distinguished indicating the occurrence of a phase separation. For volume fraction from 0.35 up to 0.85, upon occurrence of a phase separation, pure testosterone separated regions can be obtained. In Fig. 2(c), the results of equilibrium calculations for sorption of testosterone onto polymer No. 136 (vit 4 h) are shown. It can be seen that for volume fraction of testosterone in water in the range of from 0.55 up to 0.98, a miscibility gap exists denoting that for each volume faction of testosterone in water, two different compositions in polymer can be distinguished indicating the occurrence of a phase separation.

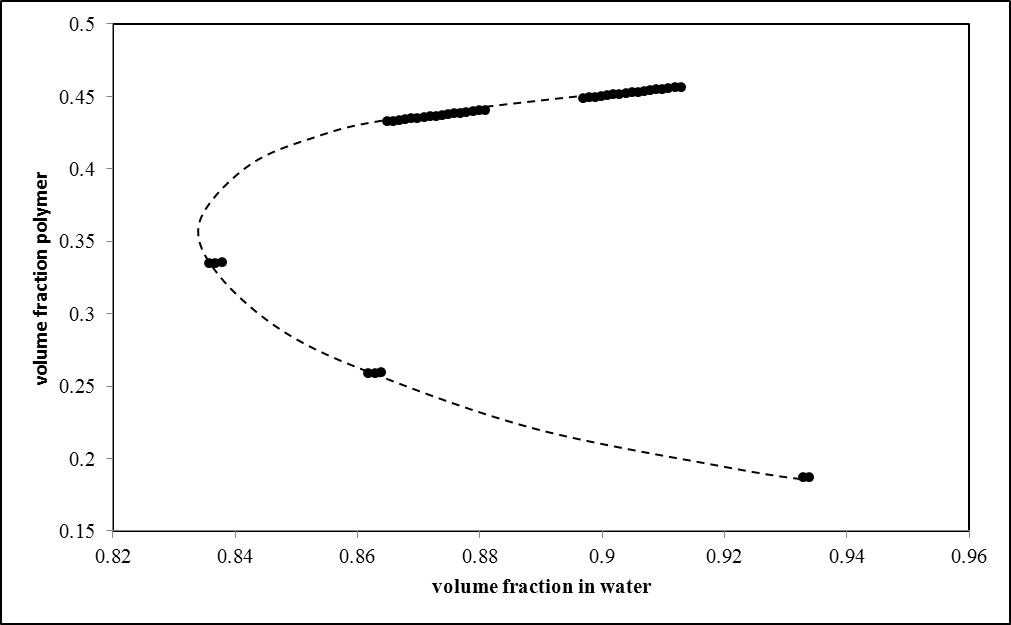


Fig. 2(a). Phase envelope for polymer No. 83 (alf an 950) and hormone No. 3 (testosterone): bullets denote calculated points and dash line shows fit

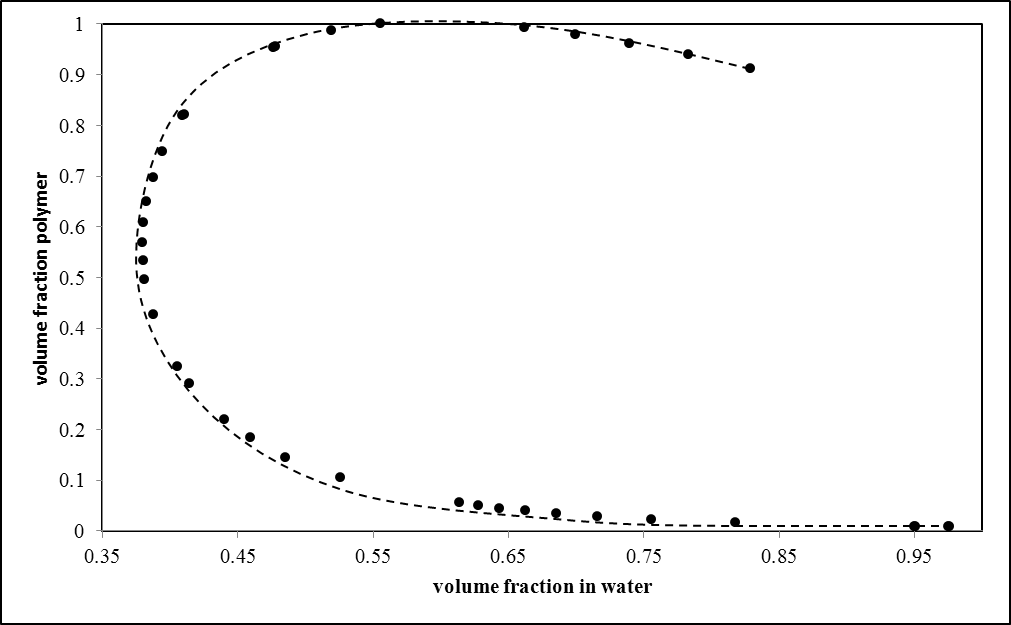


Fig. 2(b). Phase envelope for polymer No. 112 (zink silicate (cr)) and hormone No. 3 (testosterone): bullets denote calculated points and dash line shows fit

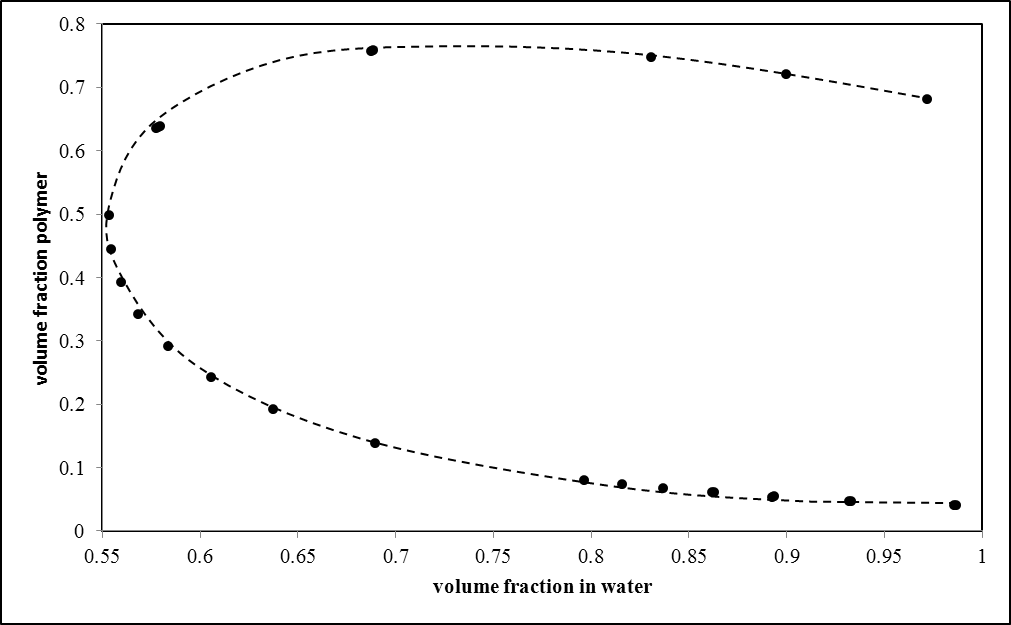


Fig. 2(c). Phase envelope for polymer No. 136 (vit 4 h) and hormone No. 3 (testosterone): bullets denote calculated points and dash line shows fit

In Fig 3(a), the results of equilibrium calculations for sorption of progesterone onto polymer No. 112 (zink silicate (cr)) are shown. It can be seen that a tight miscibility gap exists from volume faction of progesterone in water in the range of 0.36 to 0.47. If a phase separation happens, the obtained rich progesterone separated regions must be of desirable purity. As it can be seen, for a wide range of compositions i.e. beyond volume fraction 0.47, no successive sorption can be achieved. In Fig 3(b), the results of equilibrium calculations for sorption of progesterone onto polymer No. 136 (vit 4 h) are shown. It can be seen that a wide miscibility gap exists from volume faction of progesterone in water in the range of 0.46 to 0.89. If a phase separation happens, the obtained rich progesterone separated regions must be of desirable purity.

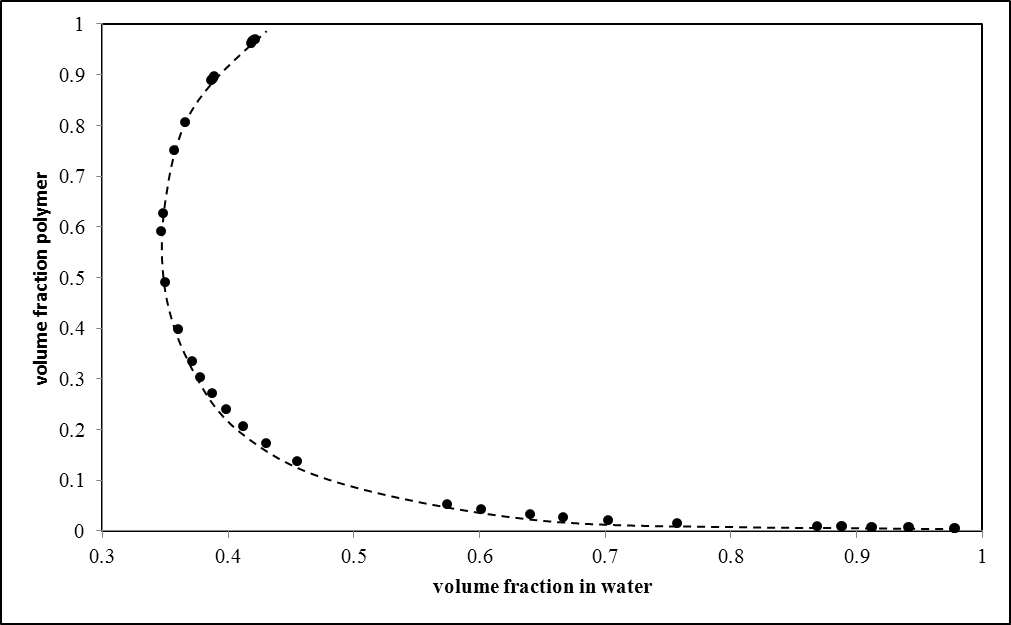


Fig. 3(a). Phase envelope for polymer No. 112 (zink silicate (cr)) and hormone No. 4 (progesterone): bullets denote calculated points and dash line shows fit

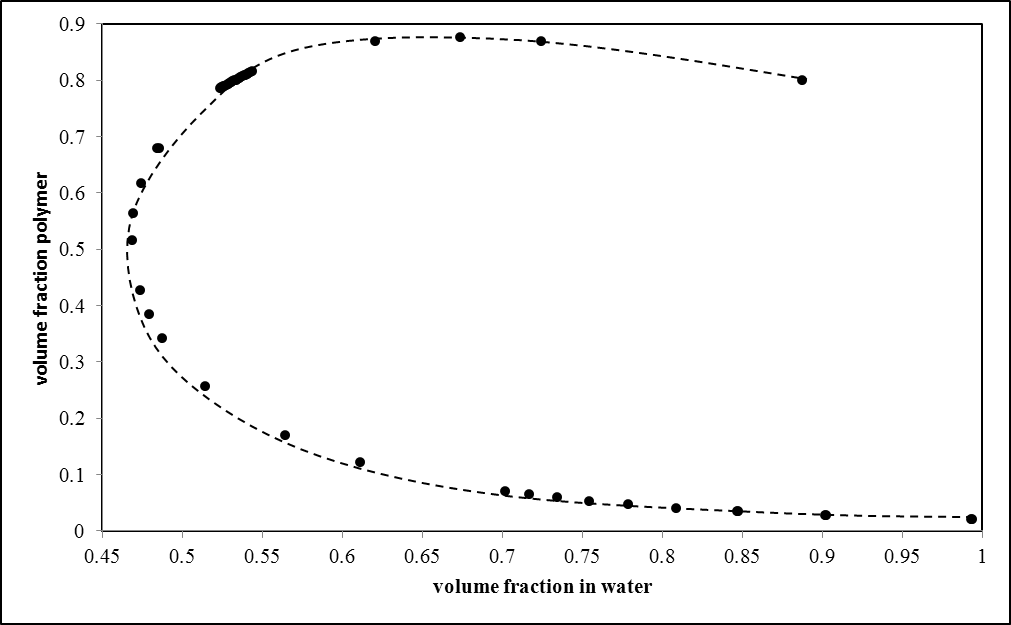


Fig. 3(b). Phase envelope for polymer No. 136 (vit 4 h) and hormone No. 4 (progesterone): bullets denote calculated points and dash line shows fit

In Fig 4(a), the results of equilibrium calculations for sorption of estriol onto polymer No. 112 (zink silicate (cr)) are shown. It can be seen that application domain of this polymer for estriol removal is highly small and tight. No acceptable removal can be achieved upon a phase separation; therefore this system cannot be advised. In Fig 4(b), the results of equilibrium calculations for sorption of estriol onto polymer No. 136 (vit 4 h) are shown. It can be seen that application domain of this polymer for estriol removal is acceptable. The phase separated Estriol region would have desirable purity. In Fig 4(c), the results of equilibrium calculations for sorption of estriol onto polymer No. 180 (pp) are shown. It can be seen that application domain of this polymer for estriol removal is acceptable. The phase separated estriol region would have desirable purity. In Fig 4(d), the results of equilibrium calculations for sorption of estriol onto polymer No. 301 (elvax eod 3602-1) are shown. It can be seen that application domain of this polymer for estriol removal is not acceptable. The phase separated Estriol region would not have desirable purity. So, this system cannot be advised. Phase envelope for polymer No. 386 (r q silicone 748) and hormone No. 5 (estriol) is shown in Fig 4(e). From the wide miscibility gap, and highly estriol rich phase separated regions, it can be concluded that upon phase separation, high purity phase separated estriol can be achieved. The sorption behavior of polymer No. 439 (lumflon lf200 30) and hormone No. 5 (estriol) is shown in Fig 4(f) indicating that increasing the estriol content of water, the sorption quantity in polymer increases. It can be readily seen that the sorption capacity of this polymer is highly limited and small and cannot be advised for estriol removal applications.

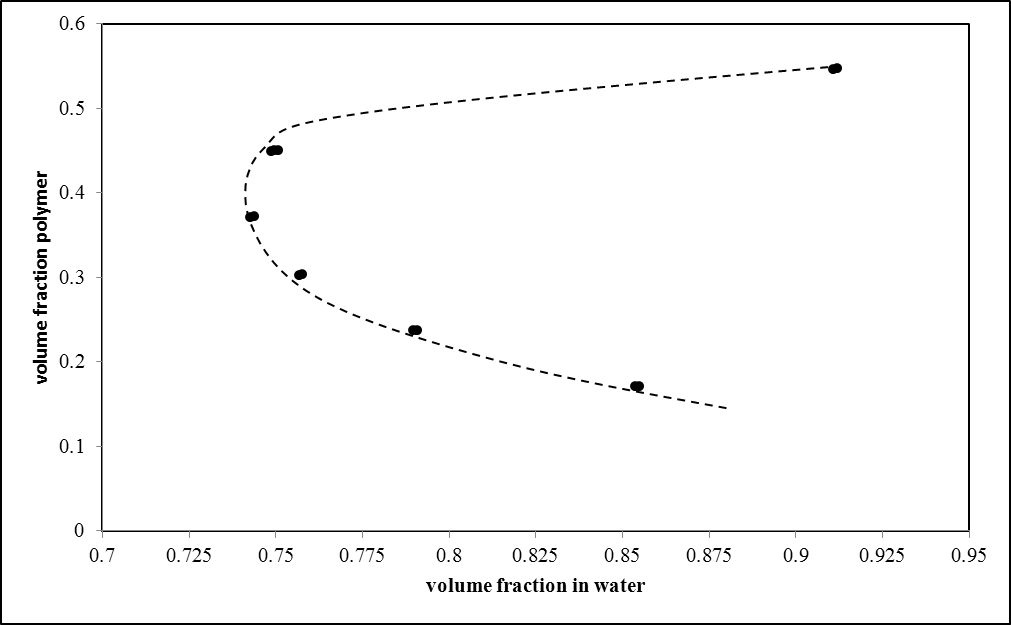


Fig. 4(a). Phase envelope for polymer No. 112 (zink silicate (cr)) and hormone No. 5 (estriol): bullets denote calculated points and dash line shows fit

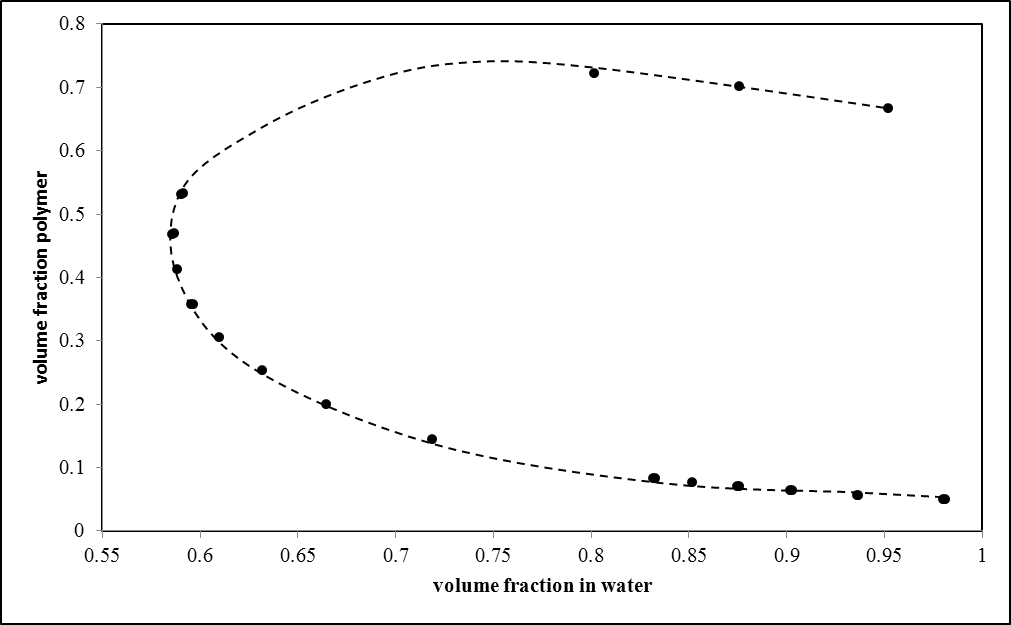


Fig. 4(b). Phase envelope for polymer No. 136 (vit 4 h) and hormone No. 5 (estriol): bullets denote calculated points and dash line shows fit

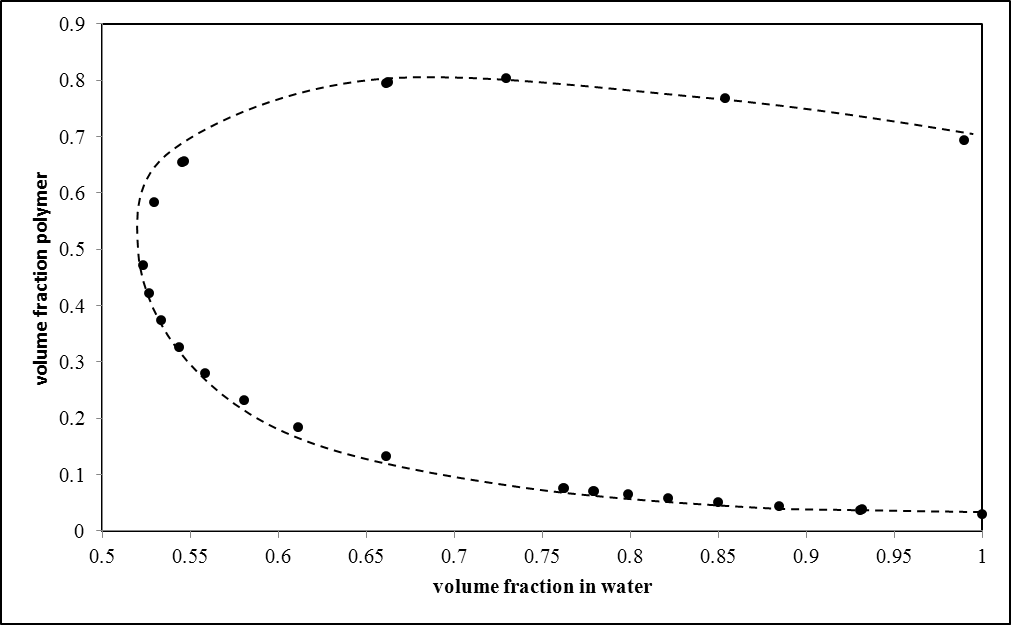


Fig. 4(c). Phase envelope for polymer No. 180 (pp) and hormone No. 5 (estriol): bullets denote calculated points and dash line shows fit

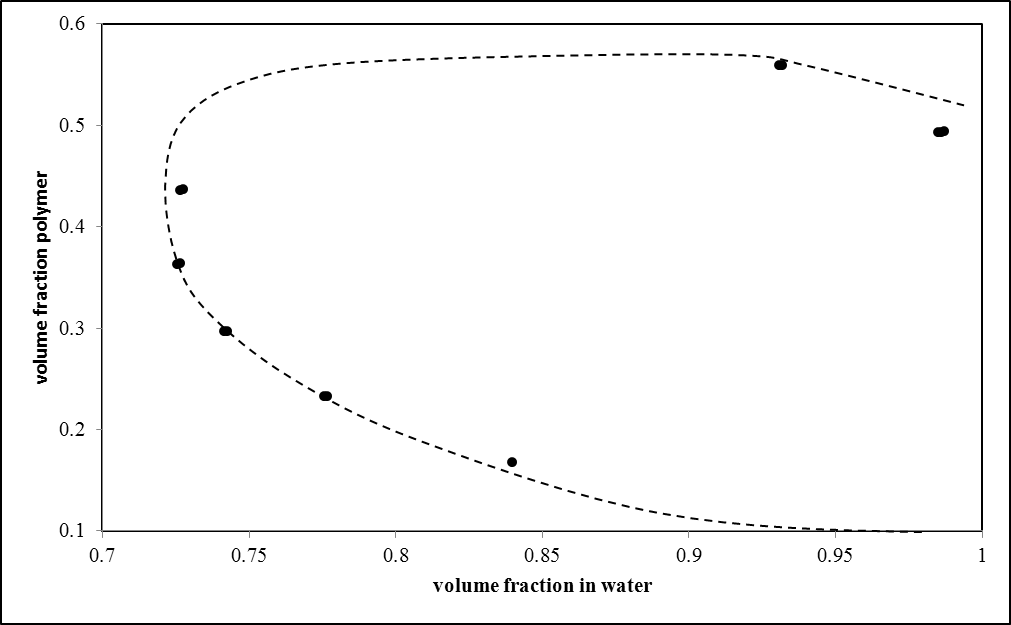


Fig. 4(d). Phase envelope for polymer No. 301 (elvax eod 3602-1) and hormone No. 5 (estriol): bullets denote calculated points and dash line shows fit

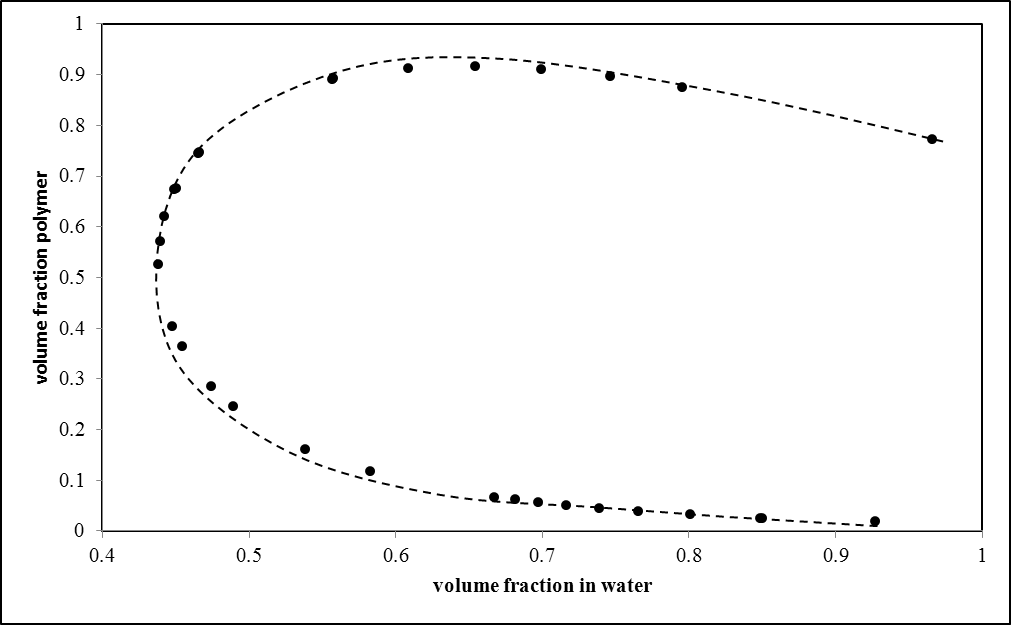


Fig. 4(e). Phase envelope for polymer No. 386 (r q silicone 748) and hormone No. 5 (estriol): bullets denote calculated points and dash line shows fit

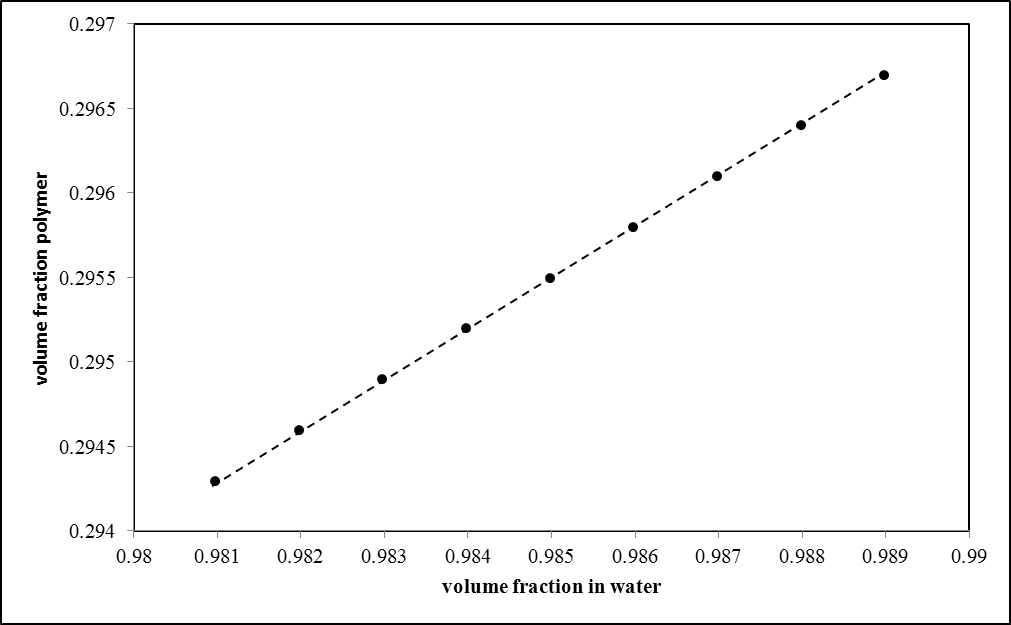


Fig. 4(f). Sorption behavior of polymer No. 439 (lumflon lf200 30) and hormone No. 5 (estriol): bullets denote calculated points and dash line shows fit

For those polymers listed in Table 3, and no separation diagram (phase envelop) is provided here, not any thermodynamic interaction was found using the aforementioned calculations. Therefore, only identifying a good pair using Hansen solubility parameters, does not guarantee that the sorption can be achieved. Here, we identified the good pairs and investigate their domain of applicability as shown above. We clearly showed the potential polymers for sorption and removal of hormones together with their removal capacity represented in terms of phase envelops.

# Conclusion

Polymeric materials have been used for various purposes in a wide range of application and industries. Nanofiltration/ultrafiltration polymeric membranes and polymeric nanosorbents substrates have been used for removal of pollutant from wastewater to increase the water quality and reduce the environmental and health risks can be emerged as a result of polluted water effluents to the ecosystem. Noting to the improvements in medical and medicine science, the consumption and utilization of harmonic drugs have been increased which might cause the problem of water streams pollution by these harmonic micropollutants. For removal of hormones from water effluent, the applications of polymeric materials through sorption mechanism of nanofiltration/ultrafiltration and/or nanosorbents have been attempted in literature where the choice of raw materials is therefore, a key step. To provide a reliable theoretical approach for feasibility analysis and performance evaluation of various polymeric materials that might be used for such water treatment studies, here, a total number of 452 polymers was collected from literature and then were analyzed and initially screened using Hansen solubility parameter to check their compatibility for selected hormone micropollutants removal. Then, for pairs which are identified as “good”, the removal equilibrium capacity was calculated using a Flory–Huggins model. While through initial screening a wide number of polymeric materials were found to be compatible for considered hormones removal, phase calculations showed that not all the good pairs identified based on Hansen solubility parameters could be used for practical separation applications.

# Supplementary file info

Table 4 includesdatabase of 452 polymers collected from Ref. [[18](#_ENREF_18)]. Table 5 includes the calculated values of Δa=|δa,1-δa,2| for polymers.

References

1. Jobling S, Nolan M, Tyler CR, Brighty G, Sumpter JP (1998) Widespread Sexual Disruption in Wild Fish. Environmental Science & Technology 32 (17):2498-2506. doi:10.1021/es9710870

2. Younes M (1999) Endocrine Disrupting Chemicals and Human HealthSpecific issues in health risk assessment of endocrine disrupting chemicals and international activities. Chemosphere 39 (8):1253-1257. doi:10.1016/S0045-6535(99)00193-9

3. Tyler CR, Jobling S, Sumpter JP (1998) Endocrine Disruption in Wildlife: A Critical Review of the Evidence. Critical Reviews in Toxicology 28 (4):319-361. doi:10.1080/10408449891344236

4. Gabriel FLP, Routledge EJ, Heidlberger A, Rentsch D, Guenther K, Giger W, Sumpter JP, Kohler H-PE (2008) Isomer-Specific Degradation and Endocrine Disrupting Activity of Nonylphenols. Environmental Science & Technology 42 (17):6399-6408. doi:10.1021/es800577a

5. Schafer AI, Akanyeti I, Semiao AJ (2011) Micropollutant sorption to membrane polymers: a review of mechanisms for estrogens. Advances in colloid and interface science 164 (1-2):100-117. doi:10.1016/j.cis.2010.09.006

6. Zuccato E, Calamari D, Natangelo M, Fanelli R (2000) Presence of therapeutic drugs in the environment. The Lancet 355 (9217):1789-1790. doi:10.1016/S0140-6736(00)02270-4

7. Schultz MM, Furlong ET (2008) Trace Analysis of Antidepressant Pharmaceuticals and Their Select Degradates in Aquatic Matrixes by LC/ESI/MS/MS. Analytical Chemistry 80 (5):1756-1762. doi:10.1021/ac702154e

8. Körner W, Bolz U, Süßmuth W, Hiller G, Schuller W, Hanf V, Hagenmaier H (2000) Input/output balance of estrogenic active compounds in a major municipal sewage plant in Germany. Chemosphere 40 (9–11):1131-1142. doi:10.1016/S0045-6535(99)00362-8

9. Williams RJ, Johnson AC, Smith JJL, Kanda R (2003) Steroid Estrogens Profiles along River Stretches Arising from Sewage Treatment Works Discharges. Environmental Science & Technology 37 (9):1744-1750. doi:10.1021/es0202107

10. Kolpin DW, Furlong ET, Meyer MT, Thurman EM, Zaugg SD, Barber LB, Buxton HT (2002) Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999−2000:  A National Reconnaissance. Environmental Science & Technology 36 (6):1202-1211. doi:10.1021/es011055j

11. Johnson AC, Sumpter JP (2001) Removal of Endocrine-Disrupting Chemicals in Activated Sludge Treatment Works. Environmental Science & Technology 35 (24):4697-4703. doi:10.1021/es010171j

12. Baronti C, Curini R, D'Ascenzo G, Di Corcia A, Gentili A, Samperi R (2000) Monitoring Natural and Synthetic Estrogens at Activated Sludge Sewage Treatment Plants and in a Receiving River Water. Environmental Science & Technology 34 (24):5059-5066. doi:10.1021/es001359q

13. Andreozzi R, Canterino M, Marotta R, Paxeus N (2005) Antibiotic removal from wastewaters: The ozonation of amoxicillin. Journal of hazardous materials 122 (3):243-250. doi:10.1016/j.jhazmat.2005.03.004

14. Pelekani C, Snoeyink VL (1999) Competitive adsorption in natural water: role of activated carbon pore size. Water research 33 (5):1209-1219. doi:<http://dx.doi.org/10.1016/S0043-1354(98)00329-7>

15. Kimura K, Amy G, Drewes J, Watanabe Y (2003) Adsorption of hydrophobic compounds onto NF/RO membranes: an artifact leading to overestimation of rejection. Journal of Membrane Science 221 (1–2):89-101. doi:10.1016/S0376-7388(03)00248-5

16. Kimura K, Amy G, Drewes JE, Heberer T, Kim T-U, Watanabe Y (2003) Rejection of organic micropollutants (disinfection by-products, endocrine disrupting compounds, and pharmaceutically active compounds) by NF/RO membranes. Journal of Membrane Science 227 (1–2):113-121. doi:10.1016/j.memsci.2003.09.005

17. Lindvig T, Michelsen ML, Kontogeorgis GM (2002) A Flory–Huggins model based on the Hansen solubility parameters. Fluid Phase Equilibria 203 (1-2):247-260. doi:10.1016/s0378-3812(02)00184-x

18. Hansen CM (2000) Hansen solubility parameters: a user’s handbook. CRC Press, Florida

19. J.M. Smith, H. Van Ness, Abbott M (2005) Introduction to Chemical Engineering Thermodynamics. 7 edn. McGraw-Hill, New York